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Los Alamos, New Mexico 87545

memorandum

TO Patrick Stanley, LATO/RF, MS A140 DATE February 23, 1993

FROM D.J. Rokop, INC-6 *JK* MAIL STOP/TELEPHONE J514/5-2640

SYMBOL INC-6-93-169

SUBJECT ANALYTICAL RESULTS FOR SEPTEMBER THRU DECEMBER PONDWATER SAMPLES

The measured results for the period September thru December, 1992, for pondwater samples are as follows:

POND ID	SAMPLE	pCiPu/L	DATE SAMPLED
A4	SW60264WC	.0022	091492
	SW60273WC	0016	102392
	SW60289WC	0061	112492
	SW60301WC	0091	121492
B5	SW60266WC	0047	091492
	SW60274WC	0055	102392
	SW60290WC	0111	112492
	SW60302WC	0062	121492
C2	SW60265WC	.0684	091492
	SW60271WC	0547	102192
	SW60291WC	.0270	112592
	SW60303WC	0241	121492
STPEFF	SW60263WC	.0011	091492
	SW60275WC	.0006	102392
	SW60292WC	.0006	112392
	SW60304WC	.0013	121492

Please distribute the report to the appropriate EG&G personnel as quickly as possible

DJR:jh

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SW-A-004590

**Actinide Determination and Analytical Support for Water
Characterization and Treatment Studies at Rocky Flats**

**Task Element A
Final Report**

**Radiochemical Analyses, Radionuclide Characterization,
and Radionuclide Treatment of Rocky Flats Pond Waters
(LATO-EG&G-91-022)**

Deliverable: 5.1.5

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EXECUTIVE SUMMARY

We have developed alpha spectroscopy and thermal ionization mass spectrometry (TIMS) measurement techniques capable of detecting $^{239+240}\text{Pu}$ and ^{241}Am at 0.01 pCi/L concentrations using 2 L water samples collected from the holding ponds at the Rocky Flats Plant (RFP). Experiments verified that alpha spectroscopy and TIMS measurement techniques were comparable at the 0.01-0.5 pCi $^{239+240}\text{Pu}$ /L concentrations. A review of the alpha spectroscopy results obtained during this study indicates that the analytical uncertainty associated with samples containing 0.01 pCi/L of $^{239+240}\text{Pu}$ or ^{241}Am is 35-50% at the 67% confidence level. The analytical uncertainty decreases to $\pm 15\%$ when 0.05 pCi/L samples are measured. Measurements of water samples traced with varying amounts of $^{239+240}\text{Pu}$ indicate that the analytical uncertainty for TIMS measurements at 0.01-0.5 pCi $^{239+240}\text{Pu}$ /L concentrations is $\pm 6\%$ at the 67% confidence level.

We also developed ultra-sensitive TIMS measurement techniques capable of detecting $^{239+240}\text{Pu}$ at the 0.001 pCi/L level and ^{241}Am at the 0.003 pCi/L level using 2 L water samples. The analytical uncertainty for TIMS $^{239+240}\text{Pu}$ measurements at 0.001 pCi/L concentrations is $\pm 50\%$. The analytical uncertainty associated with ^{241}Am measurements at 0.003 pCi/L concentrations is $\pm 50\%$.

Three plutonium and two americium chemical separation schemes were investigated. These procedures were evaluated for accuracy and sample throughput. Separation schemes were specifically developed for separating plutonium and americium from waters collected from the RFP holding ponds. These procedures are fast and produce high quality results. The procedures described above were applied in studies measuring the plutonium and americium concentrations in holding ponds A1, A2, A3, A4, B1, B2, B3, B4, B5, C1, C2 and the effluent of the water treatment plant (STPEFF). The results of these studies and their significance are discussed in detail.

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1. Introduction

This work provides answers to a variety of questions pertaining to the characterization of surface waters at the Rocky Flats Plant (RFP). The primary thrust was the development and testing of analytical procedures for measuring plutonium and americium concentrations in water samples. A summary of all chemical procedures and analytical results collected in support of this project is included in the appendices. The chemical procedures are summarized in Appendices 1-5. The TIMS measurement procedures are summarized in Appendix 6. The analytical results obtained by TIMS measurement techniques are reported in Appendix 7. The alpha spectroscopy results are reported in Appendix 8 and the alpha spectroscopy QA/QC results are reported in Appendix 9. Appendix 10 is a compilation of samples analyzed by both alpha spectroscopy and TIMS measurement techniques.

A portion of the analytical measurements was performed in support of Tasks B and C. Polzer and Essington documented the results for Task B in, "The Physical and Chemical Characterization of Radionuclides in the Surface Waters at Rocky Flats Plant" ¹. Triay documented the results for Task C in, "Report on the Effectiveness of Flocculation for Removal of ²³⁹Pu at Concentrations of 1 pCi/L and 0.1 pCi/L" ².

2. Summary of Accomplishments

2.1 Analyses Performed

Table 1 is a numerical tabulation of the analytical measurements performed in support of contract LATO-EG&G-91-022.

Table 1

Analyses Performed in Support of Contract LATO-EG&G-91-022

Purpose of Analysis	Instrumental Method	Element Analyzed	No. of Analyses
Pond Water Characterization	TIMS	Plutonium	107
Pond Water Characterization	Alpha Spectroscopy	Plutonium	162
Pond Water Characterization	Alpha Spectroscopy	Americium	31
Task B Support	TIMS	Plutonium	24
Task C Support	TIMS	Plutonium	41
Methods Development	TIMS	Americium	28
QA/QC	Alpha Spectroscopy	Plutonium	23
QA/QC	TIMS	Plutonium	42

2.2 Program Support Activities

The program support activities have previously been reported Section 2 2 lists those activities.

2.2 1 Developed approved vendors list

2.2 2 Validated purity of reagents obtained from commercial vendors

2 2 3 Developed data base for analytical results

2.3 Summary of Procedures Documented

The sample management protocols have previously been reported Section 2 3 1 lists the protocols developed in support of this project Section 2 3 2 lists the analytical procedures developed in support of this project

2.3.1 Sample Management Protocols

Chain of custody
Sample collection
Shipment of nitric acid
Sample preservation
Sample container packaging
Sample container shipment
Sample receiving
Sample distribution
Shipping container return

2.3.2 Analytical Procedure Documentation

Plutonium Separation Procedure 1 (Appendix 1)
Plutonium Separation Procedure 2 (Appendix 2)
Plutonium Separation Procedure 3 (Appendix 3)
Americium Separation Procedure 1 (Appendix 4)
Americium Separation Procedure 2 (Appendix 5)
TIMS Measurement Procedures (Appendix 6)

3 Preliminary Experiments

The statement of work required that we investigate ways to rapidly obtain accurate measurements of the actinide concentrations in the holding ponds at RFP. A series of experiments was performed to verify that the methods developed produced accurate data. Summarized below are the pertinent problems.

3.1 Sample Throughput

The RFP pond water study requires that large numbers of samples be analyzed in a timely manner. The best way to increase sample throughput is to analyze small aliquots of water by sensitive measurement techniques. The statement of work required that we investigate methods for determining plutonium and americium at the 0.05 pCi/L and the 0.003 pCi/L levels. Alpha spectroscopy and TIMS are capable of detecting plutonium and americium at the 0.05 pCi/L level from 2 L water samples. TIMS can detect plutonium and americium at the 0.003 pCi/L level from 2 L water samples. All future work for Task A was predicated upon a 2 L water sample size.

It was determined that the best way to prepare a 2 L water sample for actinide analyses was evaporation. Two liters of water can be evaporated quickly. Samples can be left unattended on a hot plate overnight. Evaporation rates increase when a stream of dry air is passed over the surface of the water. Sample evaporation is not the limiting factor for sample throughput. Sample throughput is limited by the amount of time it takes to chemically process the sample and/or the amount of instrument measurement time available.

The plutonium and americium in the waters from the holding ponds at RFP must be separated from the dissolved minerals present in the samples before they can be measured. Chemical separation and purification techniques are not 100% efficient. A portion of the plutonium and americium is lost during processing. This loss can be determined by isotope dilution measurement techniques. A known amount of "isotopically pure" ^{242}Pu and/or ^{243}Am is added to the sample prior to processing. These tracers are equilibrated with the actinides present in the sample before chemical processing is initiated. This provides a means of correcting for chemical yield so the true plutonium and americium concentrations can be determined. Sample - tracer equilibration is most easily accomplished by heating the sample in a strong mineral acid. This should be done after the sample has been concentrated and before chemical processing is initiated. It is best to add the acid prior to "boil-down." This acid digestion aids in sample-tracer equilibration and may facilitate chemical processing.

Actinide concentration by ion exchange chromatography and scavenging were investigated as potential methods for concentrating the plutonium and americium in RFP pond water samples. It was the authors' opinion that these techniques were unnecessary. The RFP pond water is a simple matrix and the actinide concentrations are easy to measure in small sample aliquots. Actinide concentration by ion exchange chromatography or scavenging techniques should be reserved for large samples having complex matrices. Ion ex-

change chromatography or ferric hydroxide scavenging are the methods of choice for isolating plutonium from 200 L samples of sea water. They are "overkill" for the RFP pond water samples. These techniques may actually jeopardize the validity of the analytical results. Concentration by ion exchange chromatography or scavenging prior to sample-tracer equilibration is risky. Scavenging techniques like the Montmorillonite-Catfloc technique reported by Triay in support of Task C work regardless of the form of the plutonium that is present and provide effective methods for removing actinides from large amounts of water. However, no significant time gain would be achieved by applying the technique to the 2 L pond water samples that are required to meet the analytical goals of this project.

3.2 Sample Homogeneity

There is an inherent pitfall in analyzing very small aliquots of water from the holding ponds at RFP. The RFP pond waters are not pure solutions. Inhomogeneities in the actinide concentrations exist. Much of the plutonium in the RFP pond water exists as particles or colloids. Therefore, it is extremely misleading to analyze a single 0.5 cc water sample by an instrumental measurement technique and then use that datum to extrapolate to the total actinide content of the holding ponds.

An experiment was conducted to determine the homogeneity of the waters in the RFP holding ponds. It was necessary to perform this experiment to ensure that analyses of 2 L water samples would provide representative results. Three 2L aliquots from a large sample of C2 pond water were analyzed for their plutonium content by TIMS. Values of 4.10×10^{-2} , 5.34×10^{-2} and 4.03×10^{-2} pCi $^{239+240}\text{Pu}$ were obtained. The coefficient of variation (CV) among the triplicate samples was 16%. A field blank consisting of deionized water was run simultaneously. This blank was handled in the field and in the laboratory in an identical manner to the C2 pond water sample. The field blank contained less than 5×10^{-4} pCi $^{239+240}\text{Pu/L}$. The homogeneity of ponds A4 and B5 were not assessed. These ponds have extremely low actinide concentrations. Determination of sample homogeneity at the 0.003 pCi/L level is very expensive, tedious and labor intensive. These measurements were beyond the scope of this study.

The 16% CV for the plutonium content of pond C2 must be considered a "snapshot-in-time" and not a hard and fast number. The majority of the plutonium in the RFP vicinity is in the soil. This plutonium may be particulate in nature or it may be present in some other form that is attached to native soil particles. When left undisturbed, the plutonium tends to bind with the soil and become less available for transport. Earthwork that disturbs the grass cover of the soil tends to increase erosion. Increased erosion transports more soil and its associated plutonium into the holding ponds. (The holding ponds were established to collect any plutonium being transported by water.) There is a finite chance that any increase in erosion rates will also increase the number of "hot particles" being introduced into the holding ponds. Sample inhomogeneity increases as the number of "hot particles" increases. Therefore, the inhomogeneity of the plutonium content of the holding ponds may vary as a function of the extent and duration of earthwork being conducted.

3.3 Sample Stability

Samples collected at RFP were shipped to Los Alamos National Laboratory (LANL) for analyses. Experiments were performed to verify that the actinide concentrations in the samples received at LANL were representative of the actinide concentrations in the samples collected at RFP. Actinides can adhere to the walls of the shipping containers. If this happens the actinide concentrations in the water can change with time. If the actinides adhere to the sample shipping container, there is a probability that they will not be transferred into the aliquot of water being analyzed. The problem may be circumvented by stabilizing the water at the time of collection. Samples were acidified in the field with nitric acid. The acid prevents the actinides from adhering to the walls of the container. The protocol used to stabilize the samples for this study is comparable to the protocol used by the Environmental Protection Agency (EPA)³. Samples stabilized by the EPA protocol remain stable for long periods of time. All analyses in support of this study were completed within approximately 3 months of sample collection. A series of experiments was performed to verify that the RFP water samples remained stable until they were analyzed. RFP pond water samples were traced with precisely determined amounts of ^{244}Pu comparable to the ^{239}Pu contents of the C2 pond waters. The ^{244}Pu was known to be in solution and in the +4 valence state. Aliquots of these samples were analyzed immediately for their ^{239}Pu and ^{244}Pu content by TIMS techniques. The remainder of the samples were stored in the laboratory. Aliquots were drawn 14 days and 73 days later for plutonium analyses. The results are shown in Table 2.

Table 2

Sample Stability Studies

R F Sample #	Separation Date	^{239}Pu Atoms/L	^{244}Pu Atoms/L	^{244}Pu Meas/Added
SW60179WC	01/07/92	$1.35 \times 10^{+9}$	$2.17 \times 10^{+9}$	0.995
SW60179WC	01/24/92	$1.30 \times 10^{+9}$	$1.97 \times 10^{+9}$	0.904
SW60179WC	03/31/92	$1.23 \times 10^{+9}$	$2.03 \times 10^{+9}$	0.931
SW60180WC	01/07/92	$1.78 \times 10^{+9}$	$2.12 \times 10^{+9}$	0.972
SW60180WC	01/24/92	$1.42 \times 10^{+9}$	$2.33 \times 10^{+9}$	1.071
SW60180WC	03/31/92	$1.36 \times 10^{+9}$	$2.16 \times 10^{+9}$	0.991
SW60181WC	01/07/92	$1.32 \times 10^{+9}$	$2.02 \times 10^{+9}$	0.927
SW60181WC	01/24/92	$1.23 \times 10^{+9}$	$2.07 \times 10^{+9}$	0.950
SW60181WC	03/31/92	$1.57 \times 10^{+9}$	$2.19 \times 10^{+9}$	1.005

The ^{244}Pu concentrations detected in each aliquot were consistent with the amount of ^{244}Pu added to the samples. The mean ratio of ^{244}Pu detected to ^{244}Pu added was $0.972 \pm 5.2\%$. The CV's for the atoms of ^{239}Pu in samples SW60179WC, SW60180WC

SW60181WC were 5%, 15% and 13% respectively. The CV's for the ^{239}Pu concentration levels measured were consistent with the 16% CV determined in the sample homogeneity study. The CV's for the atoms of ^{244}Pu in samples SW60179WC, SW60180WC and SW60181WC were 5.0%, 5.2% and 4.2% respectively. The largest (5.2%) CV for the ^{244}Pu concentrations may be indicative of the analytical uncertainty of the measurement since the ^{244}Pu was added as a true solution. Additional tests of analytical uncertainty are described in section 3.4.

Next, shipping containers originally containing C2 pond waters that were analyzed for the monthly sampling program were leached with nitric acid. No plutonium was detected in the acid at the 0.001 pCi level.

Water samples were collected for alpha spectroscopy analyses on a monthly basis. Water samples were also collected on the same day at the same location using the same protocols for alpha spectroscopy analyses in support of the quarterly survey program. This is a duplication of sampling. Often three months elapsed between the analyses of the monthly samples and the quarterly samples. A review of the americium and plutonium results from these programs indicated that the data were comparable. No statistically significant bias could be detected. These data led the authors to state that the protocols used to stabilize the pond water samples were effective.

3.4 Analytical Uncertainties

Unless stated otherwise all analytical uncertainties reported in this document are at the 67% confidence level. The analytical uncertainty associated with the alpha spectroscopy measurements includes the standard deviation of the sample activity, the standard deviation of the counter background, the standard deviation of detector efficiency for the isotope of interest, the standard deviation of the detector efficiency for the measuring the isotope dilution tracer, the standard deviation of the tracer recovery fraction, and the standard deviation of the sample quantity aliquoted. The standard deviation of the sample activity and the standard deviation of the counter background are the predominant error terms.

A series of experiments was conducted to estimate the uncertainty of the techniques used to obtain the TIMS data. A plutonium solution was prepared from the National Bureau of Standards and Technology (NIST) Standard Reference Material (SRM) 949f. This NIST certified sample was dissolved in ultra-pure nitric acid that was prepared by sub-boiling distillation. A series of dilutions was prepared. The instrumental uncertainty determined from analyses of 12 aliquots containing 0.05 pCi of plutonium was $\pm 2\%$. Next, pond C2 water samples spiked with ^{244}Pu and 2 L aliquots were analyzed to assess the uncertainties associated with the chemical processing of the samples. These ^{244}Pu results are reported in Table 2. At the present the ($\sim 6\%$) uncertainty derived from these data represents our best estimate of the overall uncertainty associated with processing holding pond waters containing 0.1 - 0.5 pCi/L of plutonium. Additional experiments are scheduled to define the uncertainties associated with the chemical processing of water samples. The

analytical uncertainty attributable to instrumental effects when measuring 0.003 pCi $^{239+240}\text{Pu}$ samples is ~ 18%

4. Plutonium

4.1 Plutonium Chemical Separation Procedures

A variety of chemical separation techniques have been developed for separating plutonium from water. Robust procedures have been developed that are capable of separating plutonium from very complex matrices. These procedures usually require an initial plutonium separation by lanthanum fluoride precipitation and/or a liquid-liquid extraction. Final purification is accomplished by a series of ion exchange chromatographic separations. This type of procedure has the most universal application, i.e., they work for almost any sample. They produce very pure samples that can be measured by alpha spectroscopy or TIMS. However, these chemical separation procedures are long and tedious. They are not amenable to high sample throughput.

Very rapid plutonium separation procedures have been developed that use a single ion exchange chromatography column. This is the type of separation procedure that is usually developed for environmental studies requiring large numbers of analyses. The principal advantage of the single chromatographic column techniques is speed. However, they do not produce extremely pure plutonium samples. Addition of ion exchange columns to a chemical separation procedure usually increases chemical purity. They also increase the amount of time required to process a sample. Single chromatographic column separation techniques usually produce samples sufficiently pure for alpha spectroscopy measurement techniques; they cannot be used to purify samples for TIMS measurements of plutonium and americium at the sub-picocurie level. No chemical separation procedure has ultimate speed and ultimate purity. Sample throughput is increased at the expense of sample purity; sample purity is optimized at the expense of sample throughput. Chemical separation techniques should be developed for each specific application. The procedure should be the best compromise between sample purity and sample throughput.

We investigated three chemical separation procedures for isolating plutonium from water samples collected from the holding ponds at RFP. They are reported in Appendices 1, 2 and 3. All three procedures are capable of isolating plutonium at the 0.01 pCi/L level. Procedures 1 and 3 are suitable for both alpha spectroscopy and TIMS measurements. Procedure 2 was developed for alpha spectroscopy measurements. Procedure 3 was specifically designed to isolate plutonium from the waters in the holding ponds at RFP. It is capable of producing samples for both alpha spectroscopy and TIMS measurement techniques. We feel that it is the best compromise between sample purity and sample throughput for the RFP pond water study.

Plutonium Separation Procedure 1 was derived from chemistry developed by Knobloch, Armijo, and Efurd.⁴ All of the data generated using this procedure is reported in Appendix 7. The procedure was specifically designed to isolate plutonium from large amounts of very complex matrix materials. The procedure uses a lanthanum fluoride precipitation,

an ethyl acetate extraction and a series of anion exchange chromatographic separations to purify the sample. This procedure produces an ultra-pure plutonium sample that can be measured by TIMS. The TIMS techniques used to obtain the plutonium measurements are documented in Appendix 6. Our TIMS procedures for plutonium analyses are published.^{5,6}

Samples prepared using Plutonium Separation Procedure 1 are also suitable for alpha spectroscopy measurements. The minimum detection limit (the 95th percentile of the background distribution) for this chemical separation procedure, using TIMS as the measurement technique, was 0.001 pCi/L when analyzing 2L water samples. Plutonium Separation Procedure 1 combined with TIMS measurements meets and significantly exceeds the requirements in the Statement of Work to develop analytical measurements for the plutonium contents of the holding ponds at the 0.05 pCi/L and the 0.003 pCi/L levels. The average plutonium recovery from 2 L water samples using this procedure is $70\% \pm 20\%$. The chemical yield decreases as the sample size increases. This procedure has been used at LANL to set an upper limit of 0.00008 pCi/L of plutonium by processing 200 L water samples. The validity of Plutonium Separation Procedure 1 and the TIMS measurement techniques was verified by analyzing samples spiked with known quantities of the plutonium SRM 949f that was certified by NIST. This procedure was used to analyze the first water samples received from RFP and it served as the reference method for evaluating the other plutonium chemical separation procedures that were investigated. The TIMS instruments used to obtain measurements were calibrated using the NIST Standard Reference Materials (SRM) U-100, (SRM) U-500, and (SRM) U-950, and SRM (Pu-949f).

Plutonium Separation Procedure 2 is a modified version of the chemical separation procedure developed by Peters, Knab, and Eberhardt.⁷ The plutonium is removed from the anion exchange column by a 0.36 M HCl - 0.01 M HF solution instead of a NaI - HCl solution. The procedure was designed to isolate plutonium from soils, water, air particulates, and biologicals for measurement by alpha spectroscopy. This procedure was used to process all of the RFP water samples analyzed by alpha spectroscopy. The results of the alpha spectroscopy measurements are reported in Appendix 8. Peters et al., state that for routine measurements with 80,000 s counting periods and a counting efficiency of 25%, the minimum detection limit (the 95th percentile of the background distribution) for $^{239+240}\text{Pu}$ is 0.02 pCi per sample. The alpha spectrometers used to measure the RFP pond water samples had higher backgrounds in the ^{238}Pu energy region than the $^{239+240}\text{Pu}$ energy region. The lower limit of detection for ^{238}Pu was approximately 0.03 pCi /L. Two liter water samples were analyzed in support of the RFP pond water study. This chemical separation technique for alpha spectroscopy measurements exceeds the requirement in the Statement of Work to develop analytical measurements for the plutonium contents of the holding ponds at the 0.05 pCi/L level. The validity of the procedure was verified by analyzing certified plutonium samples prepared by NIST, the Environmental Protection Agency (EPA) and the DOE Environmental Measurements Laboratory (EML). The gas proportional counters used to obtain the measurements were calibrated using the NIST Standard Reference Material (SRM) 4906-B17, the ^{238}Pu primary standard.

A series of "in-house" materials were prepared by pipetting known amounts of plutonium standards into water. These samples were submitted as blind QA/QC standards with each batch of RFP water samples submitted for alpha spectroscopy analyses. Analyses were considered under control if the absolute value of the difference between the results obtained by measuring the "in house" QA/QC samples and the certified mean was within the propagated standard deviation of experimental uncertainty. These QA/QC protocols are described in LANL document LA-11637-MS titled, "Quality Assurance for Health and Environmental Chemistry 1988" ⁸. The results of this QA/QC program are summarized in Appendix 9. They verify the fact that the analyses were under control during the processing of each batch of samples.

Plutonium Separation Procedure 3 was specifically developed for separating plutonium from water samples collected from the holding ponds at the Rocky Flats Plant. Analyses of the chemical composition of a water sample collected from pond C2 allowed us to specifically tailor the chemistry for these samples. The chemical composition of the water sample collected from pond C2 is shown in Table 3.

Table 3

Major Ionic Species Present in RFP Holding Pond Water

Ionic Species	Concentration (mg/L)
Ca ⁺⁺	34.0
Mg ⁺⁺	7.4
Na ⁺	29.0
K ⁺	7.0
Fe ⁺⁺⁺	<0.5
Mn ⁺⁺	<0.1
Si ⁺⁺⁺⁺	1.2
Li ⁺	<0.1
Al ⁺⁺⁺	0.1
F ⁻	0.4
Cl ⁻	34.2
SO ₄ ⁻⁻	47.4
NO ₃ ⁻	23.7

The data reported in Table 3 were used as the basis for eliminating unnecessary chemical processing steps during the development of Plutonium Separation Procedure 3. Samples can be processed by Plutonium Separation Procedure 3 in less than one fourth the time required to process samples using Plutonium Separation Procedure 1. This procedure is amenable to batch processing. Samples can be processed in batches of 6-12 by a single analyst. There are several places in the procedure where the processing can be halted overnight or longer without adverse effects. This enables the analyst to increase sample throughput by processing several batches of water samples simultaneously. The proce-

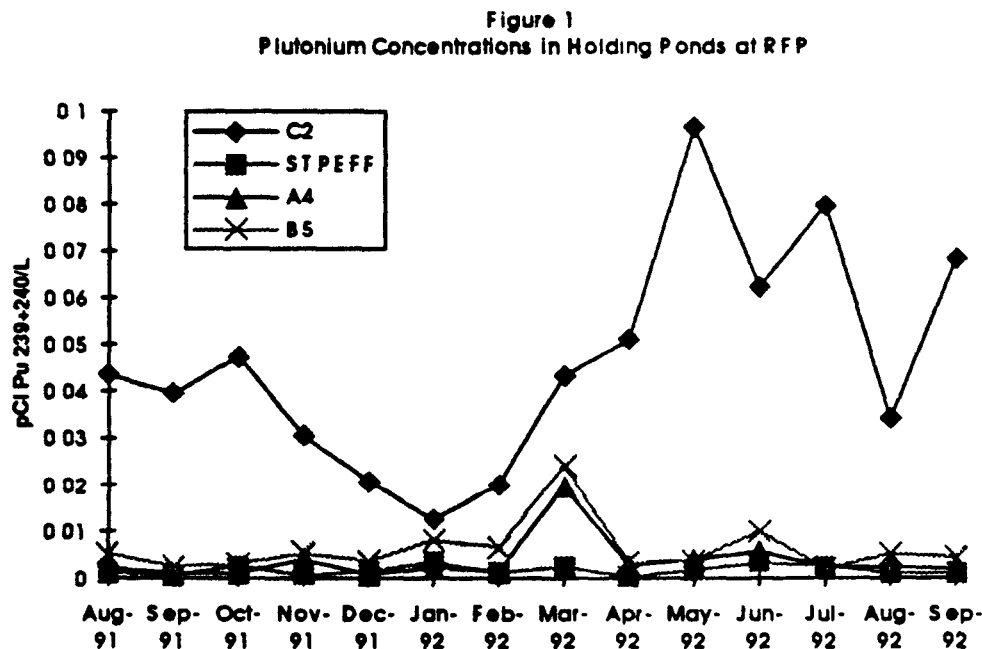
4.2 Plutonium-238 Results

The plutonium processed at RFP has a $^{238}\text{Pu}/^{239+240}\text{Pu}$ alpha activity ratio of ~ 0.04 . RFP did not process isotopically pure ^{238}Pu , all of the ^{238}Pu processed at RFP was associated with $^{239+240}\text{Pu}$. Plutonium-238 cannot be chemically fractionated from $^{239+240}\text{Pu}$ in the laboratory or the environment. Samples having a $^{238}\text{Pu}/^{239+240}\text{Pu}$ alpha activity ratio of 0.04 must contain at least 0.75 pCi/L of $^{239+240}\text{Pu}$ in order to have sufficient ^{238}Pu to be detected at the 0.03 pCi/L level when analyzing 2L water samples by alpha spectroscopy. No samples analyzed in this study had sufficiently high plutonium concentrations to obtain accurate ^{238}Pu measurements. The ^{238}Pu concentrations reported in Appendix 8 are upper limit values that verify the fact that no water samples collected during this study had ^{238}Pu levels above the 0.05 pCi/L discharge limit. Two liter water samples provide an excellent means for determining that the plutonium concentrations in the holding ponds are below the 0.05 pCi/L discharge limits. Analyses of 2L water samples are inadequate for determining the actual ^{238}Pu concentrations in the holding ponds at RFP. Aliquots ranging in size from 7.5-37.5 L would have been required from pond C2 in order to obtain sufficient ^{238}Pu for alpha spectroscopy analyses. Over 240 L water samples would have been required to quantify the actual ^{238}Pu concentrations in ponds A4 and B5. Even larger samples would have been required to measure the ^{238}Pu content, if any is present, in the effluent of the treatment plant (STPEFF). Large aliquots of water must be analyzed by chemical separation procedures that use multiple ion exchange chromatographic separations to remove the last

traces of ^{228}Th and ^{224}Ra that are naturally present in the RFP holding pond waters. If these nuclides are not completely, anomalously high ^{238}Pu values are obtained because the alpha emission energies of ^{228}Th and ^{224}Ra are almost identical to the alpha emission energy of ^{238}Pu . These procedures are tedious and very labor intensive. They are not amenable to high sample throughput.

4.2 Plutonium 239+240 Results

The $^{239+240}\text{Pu}$ data obtained by Plutonium Separation Procedure 1 and Plutonium Separation Procedure 3 using TIMS Analyses are reported in Appendix 7 and they are summarized in Figure 1.



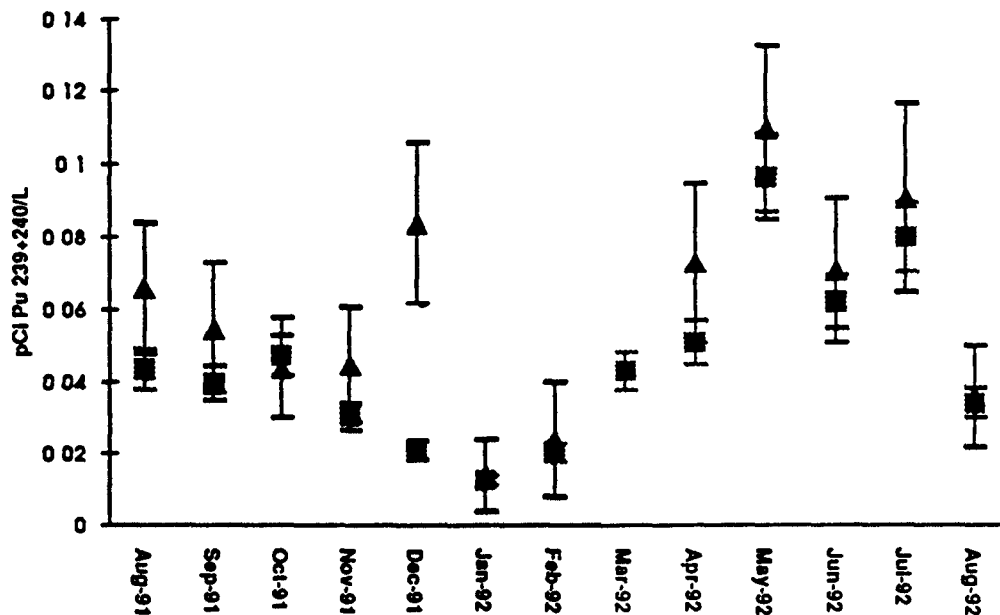
Ponds A4, B5, C2 and the effluent from the water treatment plant (STPEFF) were sampled on a monthly basis. The samples were shipped to LANL for analyses by alpha spectroscopy and TIMS. All of the monthly water samples collected from pond C2 contained sufficient plutonium for alpha spectroscopy and TIMS measurements. The plutonium concentrations in ponds A4 and B5 and the effluent from the water treatment plant were too low for alpha spectroscopy measurements. Therefore, the analytical results obtained from the monthly samplings of pond C2 served as the basis for the comparison of the measurement techniques. A 2 L aliquot of ultra-pure water was spiked with ^{242}Pu and processed simultaneously with each monthly batch of water samples. These process blanks yielded a $^{239+240}\text{Pu}$ concentration of $0.0004 \text{ pCi/L} \pm 0.0003 \text{ pCi/L}$. This processing blank made no more than a 15% contribution to measurements at the required 0.003 pCi/L minimum detection limit required by this program.

Figure 2 is a graphical representation of the plutonium concentrations in holding pond C2 as measured by alpha spectroscopy and TIMS. Water samples were collected for alpha

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spectroscopy and TIMS on the same day at the same location using identical protocols. Both sets of samples were collected, stabilized, and shipped by the protocols established for this study.

Figure 2
Comparison of Plutonium Concentrations in Pond C2 as Measured by
Alpha Spectroscopy and TIMS

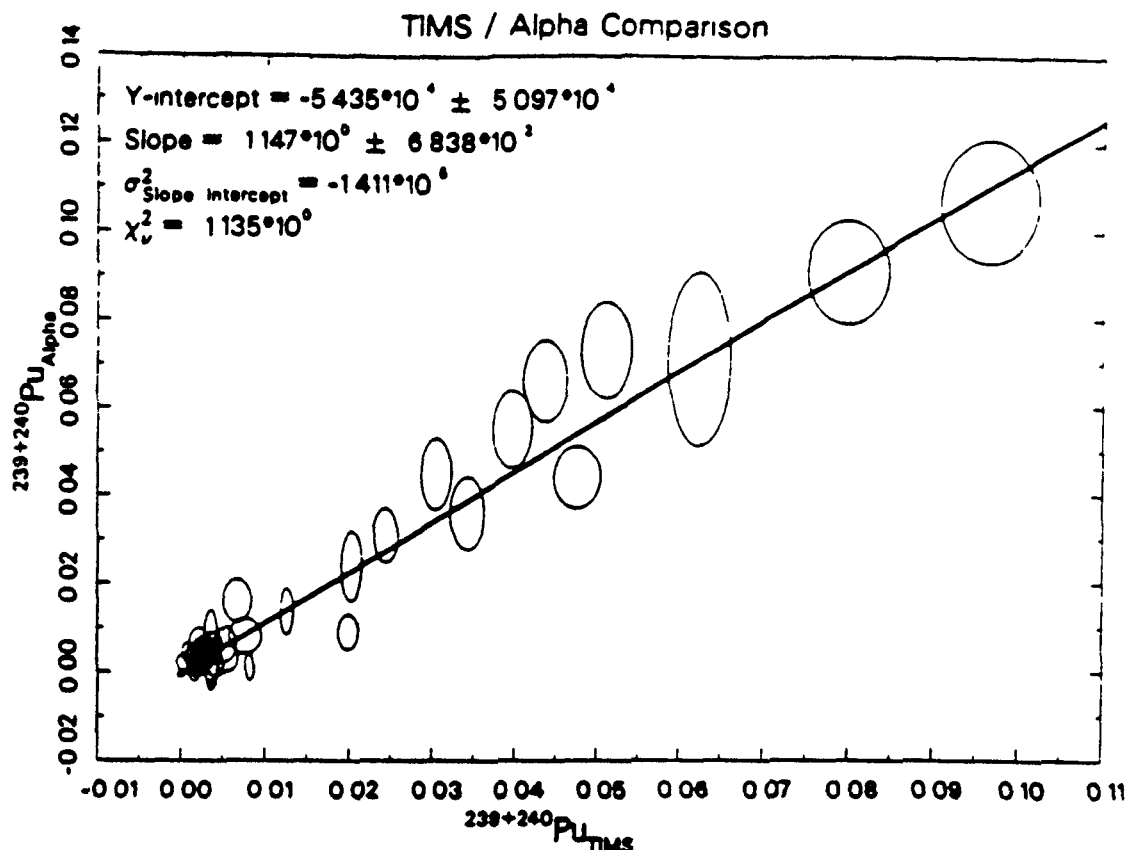


The upper and lower limit obtained by alpha spectroscopy spans the 95% confidence interval for each plutonium measurement for the monthly pond water sampling program. Eleven of the 12 sets of waters from pond C2 that were measured by alpha spectroscopy and TIMS were not significantly different at the 95% confidence level. The plutonium concentrations measured by alpha spectroscopy and TIMS in the December 1991 samples were significantly different. This may be due to the presence of a "hot particle" or the sample may have been contaminated. Insufficient data exist to confirm or refute these hypotheses.

A total of 41 RFP water samples was analyzed by alpha spectroscopy and TIMS. The analytical results are reported in Appendix 10. Figure 3 is a correlation plot of $^{239}+^{240}\text{Pu}$ measured by alpha spectroscopy versus $^{239}+^{240}\text{Pu}$ measured by TIMS. The Y-intercept of $-9.987 \times 10^{-4} \pm 2.122 \times 10^{-4}$ is not significantly different from zero. The slope is 1.151 ± 0.064 (67% confidence interval). These data indicate that there is an excellent correlation for the data obtained by alpha spectroscopy and TIMS. These data led the authors to state that alpha spectroscopy and TIMS are comparable. Either technique can be used to measure the plutonium content of water samples at the 0.01 pCi/L level.

Figure 3

Correlation plot of $^{239}+^{240}\text{Pu}$ Measurements Obtained by Alpha Spectroscopy vs TMS



A review of all of the alpha spectroscopy results obtained during this study indicates that the analytical uncertainty associated with samples containing 0.01 pCi Pu/L is 35-50%. The uncertainty decreases to 15% when 0.05 pCi Pu/L samples are measured. These uncertainties are consistent with counting statistics and are representative of the results expected from a "state-of-the-art" environmental analytical laboratory having a high sample throughput and excellent QA/QC programs. The analytical uncertainty for TMS measurements at the 0.01-0.5 pCi/L level is $\pm 6\%$. The analytical uncertainty for TMS plutonium measurements at the 0.001 pCi/L level is 35-50%. The uncertainty decreases to $\sim 16\%$ when 0.003 pCi/L plutonium samples are measured. These analytical uncertainties are representative the results expected from a "state-of-the-art" TMS measurement facility.

TMS is capable of resolving ^{239}Pu and ^{240}Pu . Table 4 summarizes the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios measured in pond C2 during the course of this investigation.

Table 4

 $^{240}\text{Pu}/^{239}\text{Pu}$ Atom Ratios Measured In Pond C2

R F Sample #	Date Sampled	$^{240}\text{Pu}/^{239}\text{Pu}$ Atom Ratio	$^{239}+^{240}\text{Pu}$ pCi/L
SW60152WC	08/28/91	0 0519	0 0436
SW60159WC	09/09/91	0 0504	0 0396
SW60163WC	10/14/91	0 0529	0 0475
SW60169WC	11/11/91	0 0526	0 0304
SW60169WC	11/11/91	0 0527	0 0316
SW60181WC	12/15/91	0 0522	0 0403
SW60200WC	01/16/92	0 0472	0 0126
SW60213WC	02/19/92	0 0523	0 0202
SW60220WC	03/18/92	0 0420	0 0433
SW60224WC	04/20/92	0 0574	0 0510
SW60232WC	05/13/92	0 0488	0 0966
SW60236WC	06/16/92	0 0565	0 0623
SW60246WC	07/29/92	0 0578	0 0799
SW60249WC	08/11/92	0 0537	0 0342
SW60260WC	08/13/92	0 0567	0 0549
SW60260WC	08/13/92	0 0587	0 0358
SW60261WC	08/13/92	0 0558	0 0405
SW60261WC	08/13/92	0 0683	0 0502
SW60262WC	08/13/92	0 0483	0 0539
SW60262WC	08/13/92	0 0426	0 0519

The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio is often useful for identifying the source term for plutonium. For example the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of the plutonium detected in pond C2 is 0 05, the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in global fallout is 0 18.⁹ Krey and Hardy have used the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in soil samples collected in Colorado to separate source terms.¹⁰ For a given sample, they were able to determine the fraction of plutonium that originated as weapons grade plutonium and the fraction of plutonium that originated as global fallout. Cobb et. al., measured the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in human lung and liver tissues collected in Colorado in an attempt to identify the source terms for any plutonium present in the tissues.¹¹ Isotopic finger printing of plutonium is frequently used in litigation.

5. Americium

5.1 Americium by Alpha Spectroscopy

Americium-241 can be detected by alpha spectroscopy or TIMS. Both measurement techniques use ^{243}Am as the isotope dilution tracer for quantifying the americium content of the sample. Samples prepared for alpha spectroscopy are traced with picocurie or less quantities of ^{243}Am . Our limit of detection by alpha spectroscopy for ^{241}Am isolated from 2 L water samples is 0.01 pCi/L using 1 day count lengths. Environmental measurement facilities typically process 0.1-2 L of water and count for 1 day. Processing larger samples and longer count lengths increase the technique's sensitivity. Larger samples require additional chemical purification and the longer counting times significantly reduce sample throughput.

We investigated two chemical separation procedures for isolating americium from water samples collected from holding ponds at RFP. These procedures are reported in Appendices 4 and 5. Americium Separation Procedure 1 was used to obtain all of the americium values presented in this report using alpha spectroscopy measurement techniques. These data are presented in Table 4.

The americium fraction of the samples processed by Plutonium Separation Procedure 2 was analyzed by Method No. ER120 which was developed by D. Knab, R. J. Peters, and W. Eberhardt.¹² The Americium Separation Procedure 1 reported in Appendix 4 summarizes the portions of Method No. ER120 used to prepare the RFP pond water samples for alpha spectroscopy analyses. The complete version of Method No. ER120 is published in LANL document LA-10300-M. Method No. ER120 is suitable for samples having less than 2 g of solid residue. The sensitivity of Method No. ER120 is limited by the background of the alpha spectrometer. For routine measurements with an 80,000-s counting period and a counting efficiency of 25%, the minimum detection limit (the 95th percentile of the background distribution) is 0.01 pCi for a 2L water sample. All of the americium values measured in this study are reported in Table 5. The values reported in Table 4 that are less than 0.01 pCi/L are below the limit of detection and are not statistically different from counter background. They are reported for completeness and to emphasize the fact that the americium content of the waters in the holding ponds are low and difficult to quantify. The average recovery for the ^{243}Am tracer is $57\% \pm 14\%$ for waters. Thorium-228, ^{224}Ra , ^{222}Rn , and ^{238}Pu interfere with ^{241}Am alpha spectroscopy determinations. The validity of the procedure was verified by analyzing certified americium samples prepared by NIST and EML. In addition EM-9 prepared in-house materials by pipetting known amounts of americium standards in water. These samples were submitted as blind QA/QC standards with each batch of RFP water samples. The result of this QA/QC program is summarized in Appendix 9. The alpha spectrometers used to obtain the measurements were calibrated to the NIST standard (SRM) 4906-B17, the ^{238}Pu primary standard. This procedure is amenable to batch processing.

Table 5

Americium Content of Holding Ponds at RFP

Pond	RFP Sample Number	Sampling Date	Alpha results pCi/L	Analytical Uncertainty
A1	SW60171WC	11/14/91	0 027	0 003
A2	SW60172WC	11/14/91	0 017	0 005
A3	SW60173WC	11/14/91	0 008	0 004
A4	SW60154WC	08/27/92	0 002	0 002
A4	SW60154WC	08/27/92	0 002	0 003
A4	SW60161WC	09/10/91	0 005	0 004
A4	SW60161WC	09/10/91	0 001	0 003
A4	SW60165WC	10/15/91	0 009	0 004
A4	SW60167WC	11/11/91	0 007	0 003
B1	SW60174WC	11/14/91	0 115	0 012
B2	SW60175WC	11/14/91	0 145	0 014
B3	SW60176WC	11/14/91	0 017	0 005
B4	SW60177WC	11/14/91	0 014	0 005
B5	SW60153WC	08/27/91	0 005	0 005
B5	SW60153WC	08/27/91	0 009	0 005
B5	SW60160WC	09/09/91	0 004	0 004
B5	SW60160WC	09/09/91	0 004	0 003
B5	SW60164WC	10/14/91	0 003	0 002
B5	SW60168WC	11/11/91	0 010	0 004
C1	SW60178WC	11/14/91	0 007	0 003
C2	SW60152WC	08/28/92	0 029	0 07
C2	SW60152WC	08/28/92	0 020	0 006
C2	SW60159WC	09/09/91	0 014	0 003
C2	SW60159WC	09/09/91	0 009	0 004
C2	SW60169WC	11/11/91	0 009	0 004
STPEFF	SW60155WC	08/27/92	0 006	0 004
STPEFF	SW60155WC	08/27/92	0 002	0 004
STPEFF	SW60162WC	09/13/91	0 009	0 005
STPEFF	SW60162WC	09/13/91	0 008	0 005
STPEFF	SW60166WC	10/15/91	0 004	0 003
STPEFF	SW50170WC	11/11/91	0 007	0 003

Thirty one water samples were analyzed for americium content. Ten of these samples had americium levels above the limit of detection of 0 01 pCi/L. No americium was detected in ponds A4 or B5. No americium was detected in the effluent from the treatment facility (STPEFF). Whenever the plutonium content of the waters increased the americium content also increased. The plutonium content of the water samples was always significantly higher than the americium content. No samples contained measurable quantities of americium and no plutonium. These facts led the authors to speculate that the americium

and plutonium were being injected into the pond by a common mechanism, i.e., transport of the particulates by water and/or wind, resuspension of sediments, and/or colloidal transport. These data do not provide information as to the mechanism of the americium and plutonium injection other than the fact that the actinides seem to be entering the water at the same time.

Table 6 lists the water samples containing measurable quantities of americium. The plutonium content and the americium to plutonium alpha activity ratios for these samples are also listed.

Table 6

Americium and Plutonium Content of RFP Waters

Pond	RFP Sample Number	241-Am (pCi/L)	239+240-Pu (pCi/L)	241-Am/239+240 Pu
A1	SW60171WC	0.027	0.058	0.466
A2	SW60172WC	0.017	0.029	0.586
B1	SW60174WC	0.115	0.218	0.528
B2	SW60175WC	0.145	0.476	0.305
B3	SW60176WC	0.017	0.061	0.279
B4	SW60177WC	0.014	0.042	0.333
B5	SW60168WC	0.010	0.055	0.182
C2	SW60152WC	0.029	0.066	0.439
C2	SW60152WC	0.020	0.066	0.303
C2	SW60159WC	0.014	0.055	0.225

The analytical uncertainties associated with the americium concentrations measured in the 2L water samples analyzed from the holding ponds ranged from 7.5-50%. The analytical uncertainties associated with the alpha spectroscopy measurements of the plutonium fractions ranged from 6.5-23%.

The americium to plutonium alpha activity ratio in materials processed at RFP is not constant. The ratio ranges from 0.2-0.4. This variation is explained by the fact that different batches of plutonium contain different amounts of ^{241}Pu . Plutonium-241 decays with a 14.4 year half life into ^{241}Am . Therefore, the americium to plutonium alpha activity ratio varies as a function of the ^{241}Pu content and age of the material. It is interesting to note that the average americium to plutonium alpha activity ratio as determined by the 10 measurements reported in Table 5 is 0.365 ± 0.133 . This alpha activity ratio is consistent with the alpha activity ratio of materials processed at RFP. It is not significantly different from the americium to plutonium alpha activity ratio of 0.2 ± 0.02 , the $^{241}\text{Am}/^{239+240}\text{Pu}$ alpha activity ratio decay corrected to December 15, 1992, measured in the NIST Standard Reference Material 4353 Rocky Flats Soil Number 1. The $^{241}\text{Am}/^{239+240}\text{Pu}$ alpha activity ratio measured in the C2 holding ponds in 1988 was 0.5 ± 0.3 .¹³ No excess americium relative to plutonium was detected in the water samples.

measured at LANL. If one assumes that the americium to plutonium alpha activity ratio measured in STPEFF is the same as that of the water in the holding ponds and that the plutonium concentrations in STPEFF measured by TIMS are correct, one would have to process 15-100 L of water to obtain alpha spectroscopy measurements of the americium content in STPEFF instead of an upper limit.

Polzer and Essington reported in their Task B summary that a significant fraction of the plutonium in waters collected from pond C2 was soluble and passed through a 0.02- μ m filter. Therefore, it is conceivable that the americium and plutonium can chemically fractionate. Americium exists in the +3 valence state. Plutonium exists in the +4 or higher valence state in nature. These differences in valence may allow the americium and plutonium to fractionate. The data summarized in Table 5 suggests that the amount of chemical fractionation, if any exists, is small and may be very difficult to detect. The americium to plutonium alpha activity ratio measured in this study was consistent with the activity ratio of materials processed at RFP. These facts led the authors to postulate that elaborate experiments requiring the processing of hundreds of liters of pond water would be required to study any americium/plutonium chemical fractionation phenomenon that may be occurring in the holding ponds. Analysis of 1-10 L water samples for chemical fractionation studies is an exercise in futility.

5.2 Americium by TIMS

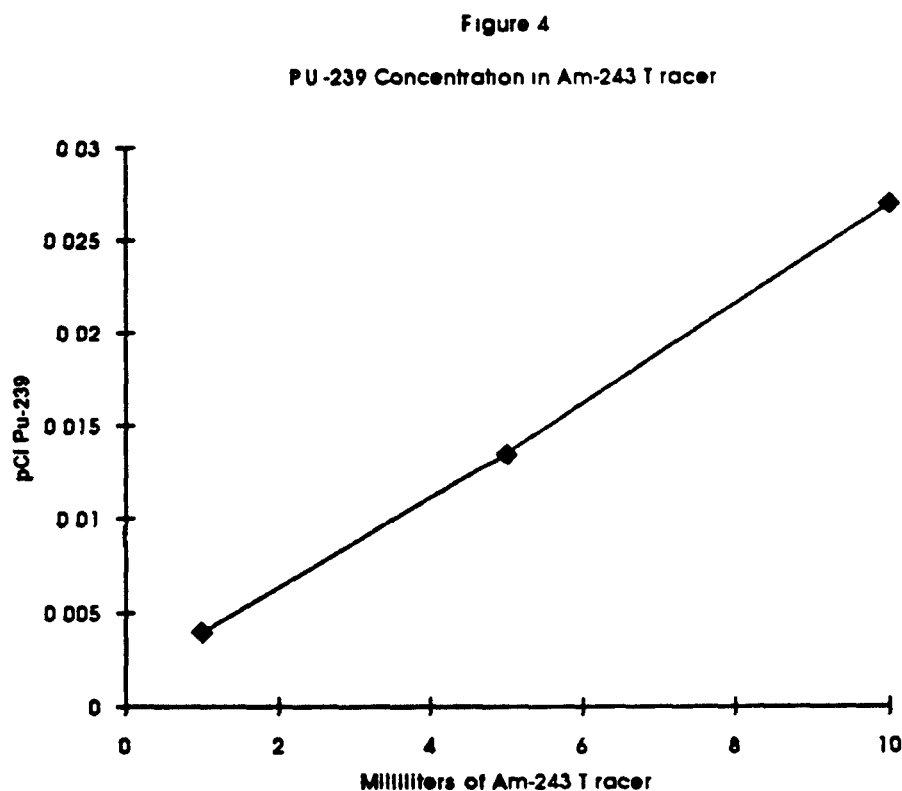
Americium Separation Procedure 2 was specifically designed to isolate americium from waters collected from the holding ponds at RFP. Americium Separation Procedure 1 may leave traces of the lanthanide elements in the sample. These trace impurities do not affect alpha spectroscopy measurements. However, they have a deleterious effect when samples are analyzed by TIMS. We developed chemistry specifically designed to optimize TIMS measurements. The procedure is amenable to batch processing.

For TIMS analyses the americium is separated from thorium and plutonium on an anion exchange column using 7.5 M HNO_3 . Next, americium is extracted from 12 M HNO_3 into Dibutyl-N,N-Diethylcarbamolphosphonate (DDCP) and back-extracted into 6 M HCl . This step removes uranium, radium, and calcium. Final purification is accomplished on two anion exchange columns using acetone-hydrochloric acid. These columns separate americium from the lanthanide elements. Preliminary experiments using water collected at RFP from pond C2 indicate that this separation procedure has a 65% chemical yield. Measurements of water samples traced with varying amounts of americium indicate that the analytical uncertainty for TIMS measurements at the 0.05 pCi/L level is $\pm 6\%$. The uncertainty associated with americium measurements at the 0.003 pCi/L level is 50%. Initiation of a mixed waste ban at LANL prevented further refinement of this procedure.

Our TIMS analysis technique requires that samples be traced with 100 pg (346 pCi) of ^{243}Am . Analyses of samples spiked with americium verified that TIMS is capable of detecting ^{241}Am in a 2 L water sample at the 0.003 pCi/L level. The 100 pg of ^{243}Am required for TIMS presents a problem whenever americium and plutonium are analyzed.

from the same aliquot of water because the alpha decay product of ^{243}Am is ^{239}Pu . Plutonium samples traced with ^{243}Am must have the plutonium measurements corrected for the ^{239}Pu present in the americium tracer. Experiments were conducted to determine the feasibility of correcting the plutonium concentrations in RFP pond waters traced with ^{242}Pu and ^{243}Am . The results of these experiments are summarized below.

One, 5 and 10 mL aliquots of the ^{243}Am tracer solution prepared for TIMS analyses were spiked with ^{242}Pu . The plutonium was isolated and measured by thermal ionization mass spectrometry to determine the amount of ^{239}Pu present in the ^{243}Am . The results are shown in Fig. 4.



These data indicate that the ^{239}Pu content of the ^{243}Am tracer was 0.0027 pCi/mL ^{243}Am spike on June 23, 1992.

Two-liter samples of the pond waters collected in May and June were traced with 1 mL of ^{243}Am tracer and the standard amount of ^{242}Pu tracer used in these studies. Separate aliquots were traced with ^{242}Pu only. The results obtained for this study are reported in Table 7.

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Table 7

Water Samples Traced With ^{242}Pu And Water Samples Traced With ^{242}Pu and ^{243}Am

Sample #	Pond	^{242}Pu Tracer	^{243}Am Tracer	pCi Pu/L Observed	pCi Pu/L *Corrected
SW60222WC	A4	X		0 0029	0 0029
SW60222WC	A4	X	X	0 0050	0 0023
SW60230WC	A4	X		0 0041	0 0041
SW60230WC	A4	X	X	**LIA	**LIA
SW60223WC	B5	X		0 0036	0 0036
SW60223WC	B5	X	X	0 0057	0 0030
SW60231WC	B5	X		0 0040	0 0040
SW60231WC	B5	X	X	0 0084	0 0057
SW60225WC	STP EFF	X		0 0005	0 0005
SW60225WC	STP EFF	X	X	0 0060	0 0033
SW60233WC	STP EFF	X		**LIA	**LIA
SW60233WC	STP EFF	X	X	0 0045	0 0018
SW60224WC	C2	X		0 0510	0 0510
SW60224WC	C2	X	X	0 0521	0 0494
SW60232WC	C2	X		0 0966	0 0966
SW60232WC	C2	X	X	0 1010	0 0983

*The pCi Pu/L corrected values reported were calculated by subtracting the 0 0027 pCi Pu/g of ^{243}Am tracer from the observed value obtained from the analyses of the aliquots of water spiked with both ^{242}Pu and ^{243}Am . The samples traced with ^{242}Pu only do not require this blank correction.

**LIA = The sample was lost in analysis

The C2 pond water aliquots traced with ^{242}Pu and the C2 pond water aliquots traced with ^{242}Pu and ^{243}Am provide comparable results once the plutonium contribution from the ^{243}Am tracer is subtracted. However, the addition of 1 mL of the ^{243}Am tracer significantly increased the amount of plutonium observed in the waters collected from ponds A4, B5, and STP EFF relative to previous amounts measured in the ponds using aliquots of water traced only with ^{242}Pu . The plutonium contribution from the ^{243}Am decay continues to increase as the americium decays. Failure to remove the plutonium from the americium tracer would mean that an ever increasing ^{239}Pu contribution would have to be subtracted. If the plutonium is not removed from the tracer during the next

two years, this correction will be three times larger than the amount of plutonium currently estimated to be present in the water in ponds A4, B5 and STPEFF. Subtracting a blank increases the overall uncertainty associated with the measurements. The removal of ^{239}Pu from the ^{243}Am and subsequent restandardization of the tracer by mass spectrometric measurement techniques is very labor intensive and expensive.

The results summarized above led the authors to conclude that plutonium and americium can be analyzed by TIMS from the same aliquot of water without deleterious effects whenever the plutonium concentration is above 0.01 pCi/L. It is more cost effective and more accurate data are obtained by analyzing separate aliquots of americium and plutonium whenever the plutonium content of the sample is less than 0.01 pCi/L.

6.0 General Observations

Plutonium can be measured at the 0.01 pCi/L level by alpha spectroscopy or TIMS. Alpha spectroscopy is the only technique that we know that can consistently and accurately measure ^{238}Pu . TIMS is the only technique that we know that can consistently and accurately measure plutonium concentrations at the 0.003 pCi/L level. TIMS can measure both ^{239}Pu and ^{240}Pu .

Americium can be measured in RFP holding pond waters at the 0.05 pCi/L level by alpha spectroscopy or TIMS. Alpha spectroscopy is simpler and more cost effective. TIMS should be reserved for ultra low level measurements that are below the limits of detection by alpha spectroscopy.

Chemical processing of RFP water samples for alpha spectroscopy and TIMS measurements is comparable. It takes the same amount of time to process a sample for alpha spectroscopy as it takes to process a sample for TIMS.

7.0 Summary

We have developed analytical techniques capable of measuring plutonium and americium at the 0.01 pCi/L level using both alpha spectroscopy and TIMS. Experiments were performed to verify that the measurement techniques produced comparable results at the 0.01 pCi/L level. TIMS measurement techniques were developed to measure plutonium at the 0.001 pCi/L level and americium at the 0.003 pCi/L level. These techniques were used to measure actinide concentrations in water samples collected from holding ponds A1, A2, A#, A4, B1, B2, B3, B4, C1, C2, and the effluent from the water treatment plant.

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Plutonium Separation Procedure 1

Separation and Purification of Plutonium for Mass Spectrometric Measurement

A INTRODUCTION

This separation scheme is used to isolate sub-picocurie quantities of plutonium from large samples having complex matrices. The major steps in the procedure include (1) a fluoride precipitation, (2) an ethyl acetate extraction, (3) an anion exchange column using 0.1 M H_2SO_4 , and (4) an anion exchange column using $\text{HCl-H}_2\text{O}_2$.

B PROCEDURE

1. Add ^{242}Pu tracer to the 600 mL Teflon beaker
2. Add 500 mL of the water sample and 30 mL of HClO_4 to the beaker and start the evaporation process using a hot plate
3. Continue adding water to the beaker until a total of 2000 mL of water is evaporated
4. Add 30 mL HNO_3 and 30 mL of HClO_4 and evaporate to soft dryness
5. Add 300 mL of 3 M HCl and 5 mg of lanthanum carrier
6. Warm on a hot plate for at least one hour
7. Add 4 grams of hydroxylamine hydrochloride to the sample solution. Wait 5 minutes and add 40 mL HF
8. Turn off the hot plate and let the precipitate settle overnight
9. Centrifuge the sample solution in a 50 mL polyethylene centrifuge tube. Discard the supernate.
10. Transfer the precipitate into a 100 mL Teflon beaker and add 10 mL HNO_3 and 10 mL HClO_4 . Fume to dryness to remove any residual HF
11. Transfer the residue from the Teflon beaker with two 4 mL portions of 2 M HNO_3 into a 50 mL glass centrifuge tube. Saturate the solution with ammonium nitrate

- 12 Add 10 mL of the pre-equilibrated ethyl acetate solution to the tube, cap the tube with a size 12 Red Cap, and mix the sample for 1 minute. Centrifuge and transfer the ethyl acetate layer to another 50 mL glass centrifuge tube
- 13 Repeat step 12 two additional times combining the ethyl acetate extractions
- 14 Wash the ethyl acetate solution by adding 3 mL of pre-equilibrated 2 M HNO_3 and mixing for one minute. Centrifuge and discard the aqueous layer. Repeat the wash a second time
- 15 Back-extract the plutonium from the ethyl acetate solution by adding 8 mL of Type-1 reagent grade water and mixing for one minute. Centrifuge and transfer the aqueous layer to a clean 50 mL glass centrifuge tube
- 16 Repeat the back-extraction two more times and combine the aqueous layers. Discard the ethyl acetate
- 17 Evaporate the aqueous solution containing the plutonium to dryness. Destroy any residual ammonium nitrate remaining in the centrifuge tube by adding 2 mL of aqua regia and evaporating to dryness
- 18 Add 1 mL of 0.1 M H_2SO_4 to the tube to dissolve the plutonium (See Note 1). Load the sample onto an anion-exchange column that has been preconditioned with 2 mL of 0.1 M H_2SO_4 (See Note 2). Rinse the tube with 1 mL of 0.1 M H_2SO_4 and add the rinse to the column
19. Rinse the column with two 1 mL additions of H_2O_2 -HCl reagent. Allow the column to drain completely between each H_2O_2 -HCl addition
- 20 Rinse the column with two 1 mL portions of the HF-HCl solution. Rinse the tip of the column with a stream of deionized water. Discard the eluant
- 21 Elute the plutonium into a 50 mL glass centrifuge tube with three 0.5 mL additions of HI-HCl reagent. Allow the column to drain completely between each addition
22. Evaporate the solution to dryness
- 23 Add 6 drops of HNO_3 and evaporate to dryness. Add 6 drops of HCl and evaporate to dryness.
- 24 Dissolve the sample in 1 mL of H_2O_2 -HCl solution and load it onto an anion column that has been preconditioned with 2 mL of the H_2O_2 -HCl solution. Rinse the tube with 1 mL of the H_2O_2 -HCl solution and pass it through the column. Wash the column with 2 mL of 8M HNO_3 . Rinse the tip of the column with deionized water and discard the eluant.

- 25 Elute the plutonium into a clean 10 mL quartz test tube using three 1 mL additions of concentrated HBr. Allow each HBr addition to drain completely before adding the next.
- 26 Slowly evaporate the HBr solution to dryness.
- 27 Add 4 drops of HNO_3 and 4 drops of HClO_4 . Heat at 130°C for one hour. Raise the temperature to 180°C and continue evaporating to dryness. Cool to room temperature and cap the quartz tube.
- 28 Submit the sample for mass spectrometric analyses.

Note 1 Care must be taken to avoid concentration of the H_2SO_4 . Half molar sulfuric acid can remove 100% of the plutonium from the column.

Note 2 All columns used in this procedure are made from disposable automatic pipette tips, approximately 7 cm long and 5 mm i.d. A plug of prewashed quartz wool is placed in the tip and resin is added to a depth of 2 cm.

C REAGENTS

^{242}Pu Tracer (2 ng/mL in 2 M HNO_3 , calibrated to NIST standard 949f)

HClO_4 conc

HNO_3 conc, 8M, 2M

HBr 47% (unstabilized)

HI 48% (unstabilized)

HCl conc

H_2SO_4 0.1M

Aqua regia 3:1 mixture, by volume, of conc HCl and conc HNO_3

HI-HCl mixture 1:9 mixture, by volume, of 48% HI and conc HCl

H_2O_2 -HCl reagent 2 drops of 30% H_2O_2 to 10 mL conc HCl

HF-HCl reagent; 0.06 M HF in conc HCl

NH_4NO_3 , solid

Bio-Rad macroporous anion exchange resin AGMP-1, 50 to 100 mesh

This resin is pretreated by warming overnight in a mixture of 50%

conc HCl and 50% Type 1 reagent grade water. It is washed 20 times with

Type 1 reagent grade water and stored as an aqueous slurry.

Lanthanum carrier 5 mg La/mL H_2O

Pre-equilibrated ethyl acetate and 2M HNO_3 . These reagents are prepared by mixing a 50-50 mixture of 2M HNO_3 (saturated with ammonium nitrate) and ethyl acetate in a 1000 mL separatory funnel for 5 minutes and then separating the two layers into their respective containers.

Plutonium Separation Procedure 2

Analyses of Plutonium by Alpha Pulse Height Analyses Techniques

A. INTRODUCTION

This is a summary of the salient portions of a plutonium separation procedure for water samples which was developed by R J Peters, D Knab, and W Eberhardt of the Environmental Measurement Group (EM-9) at Los Alamos National Laboratory (LANL). The complete procedure is titled "Plutonium in Environmental Matrices - Alpha Spectrometry," and is published in the LANL document LA-10300-M

B. CHEMICAL SEPARATION PROCEDURE

- 1 Place tracer(s), an aliquot of the water sample and 10 mL of concentrated HNO_3 in a Pyrex beaker and begin the evaporation process using a hot plate
- 2 Continue adding water to the beaker until a total of 2000 mL of water is evaporated to dryness
- 3 Add 20 mL of concentrated HNO_3 and heat to boiling. When the sample begins steaming, **CAREFULLY**, add 6 drops of 48% HF while swirling the sample. Evaporate to dryness
- 4 Wash down the sides of the beaker with 10 mL of concentrated HNO_3
- 5 While heating the sample, add 30% H_2O_2 by drops until all organic materials are decomposed
- 6 Dissolve the residue in 20 mL of concentrated HNO_3 , carefully washing down the sides of the beaker
- 7 Add 5 mL of concentrated HCl to the beaker and evaporate to approximately 10 mL. Remove the sample from the hot plate and cool to room temperature
- 8 Add 100 mL of 7.2 M HNO_3 and 1 mL of saturated H_3BO_3 to the sample
- 9 Add 1 mL of NaNO_2 solution and mix thoroughly. Allow the sample to stand at room temperature for approximately 1 hour
10. Pour the sample solution through the resin column keeping the reservoir filled with approximately 40 mL of solution (See notes 1 and 2)
- 11 Wash the column with three 40 mL aliquots of 7.2 M HNO_3

- 12 Wash the column with two 20 mL aliquots of 8 M HCl. Allow each aliquot to drain to the top of the glass wool plug.
- 13 Elute the plutonium into a new 100 mL beaker with four 20 mL aliquots of 0.36 M HCl - 0.01 M HF solution.
- 14 Add 1 mL of concentrated HNO_3 to the plutonium eluate and evaporate to dryness.
- 15 Add 1 mL of concentrated HNO_3 and 5 mL of concentrated HCl to the residue and evaporate to just dry. Let the last few drops air dry to avoid baking the sample. Repeat this step if visible residue remains.
- 16 Add 5 mL of concentrated HCl and evaporate using low heat until first dry spots appear.
- 17 Wash down the sides of the beaker with 5 mL of concentrated HCl.
- 18 Cover the sample with plastic wrap and store for at least 24 hours before electroplating.

ELECTRODEPOSITION PROCEDURE

- 1 Clean the stainless steel planchet with methyl alcohol and assemble the electroplating cell.
- 2 Evaporate the sample solution on medium heat until a dry spot appears that cannot be covered by swirling the beaker.
- 3 Add 3 mL of 4% ammonium oxalate solution to the beaker. Transfer this solution to an electrodeposition cell with 0.1 M HCl until the cell is approximately half filled.
- 4 Electroplate for 30 minutes at 1 A.
- 5 While the current is still on, quench the reaction by filling the cell with 1% NH_4OH .
- 6 Empty the cell and rinse the stainless steel planchet with water followed by methyl alcohol.
- 7 Heat the planchet to a dull red color in the flame of a Bunsen burner.

Note 1. The anion exchange chromatography column used in the procedure is a glass column 197 mm long x 11 mm o. d. that tapers to a 5 mm o. d. outlet. The top of the column is equipped with a 102 mm long x 40 mm o. d. reservoir. The bottom of the column is plugged with glass wool. The column is filled with AG 1 x 4, 50-100 mesh, chloride form anion exchange resin. The resin is pre-conditioned with three 20 mL aliquots of 7.2 M HNO_3 .

Note 2. If the americium content is also to be analyzed on the sample, save the recovered sample solution from step 10 and the first 40 mL of 7.2 M HNO₃ wash from step 11 of the chemical separation procedure

D REAGENTS

²⁴²Pu tracer

²⁴³Am tracer if americium analyses is required

H₂O₂ 30%

HNO₃ conc, 7.2 M

HCl conc, 8 M, 1 M, 0.1 M

HF 48%

NH₄OH 1%

H₃BO₃ saturated

NaNO₂ 1 M

HCl-NaI reagent: Dissolve 2 g NaI in 2000 mL of 1 M HCl. Prepare fresh daily

Ammonium oxalate 4% Prepare fresh monthly

Methyl alcohol

Plutonium Separation Procedure 3

by
D. W. Efurd and F. R. Roensch

Separation and Purification of Plutonium from Rocky Flats Water Samples

A INTRODUCTION

This separation technique was specifically developed for separating plutonium from water samples collected from the holding ponds at the Rocky Flats Plant. The procedure is rapid and produces no mixed waste. The plutonium is separated and purified by a series of anion exchange columns.

B PROCEDURE

1. Add ^{242}Pu tracer, 800 mL of the water sample and 30 mL of HClO_4 to a 1000 mL glass beaker and begin the evaporation process using a hot plate.
2. Continue adding water to the beaker until a total of 2000 mL of water is evaporated.
3. Add 30 mL of HClO_4 and 30 mL HNO_3 and evaporate to soft dryness.
4. Add 30 mL of HNO_3 and evaporate to near dryness, i.e., 0.5-1.5 mL.
5. Dissolve the sample in 20 mL of 8 M HNO_3 .
6. Pass the solution through an anion exchange column that has been preconditioned with 20 mL of 8 M HNO_3 . (See notes 1 and 2).
7. Rinse the beaker with 10 mL of 8 M HNO_3 and pass the rinse through the column.
8. Rinse the column with 10 mL of 8 M HNO_3 .
9. Elute the plutonium into a clean 40 mL glass centrifuge tube by passing 10 mL of 0.5 M HCl and 10 mL of HI-HCl solution through the column.
10. Evaporate the 20 mL of solution collected in step 9 to dryness.
11. Add 2 mL of aqua regia and evaporate to dryness.
12. Add 1 mL of 0.1 M H_2SO_4 to the tube to dissolve the plutonium.

- 13 Load the sample onto an anion-exchange column that has been preconditioned with 2 mL of 0.1 M H_2SO_4 . Rinse the tube with 1 mL of 0.1 M H_2SO_4 and add the rinse to the column.
- 14 Rinse the column with two 1 mL additions of H_2O_2 -HCl reagent. Allow the column to drain completely between each H_2O_2 -HCl addition.
- 15 Rinse the column with two 1 mL portions of the HF-HCl solution. Rinse the tip of the column with a stream of deionized water. Discard the eluant.
- 16 Elute the plutonium into a 50 mL glass centrifuge tube with three 0.5 mL additions of HI-HCl reagent. Allow the column to drain completely between each addition.
- 17 Evaporate the solution to dryness.
- 18 Add 6 drops of HNO_3 and evaporate to dryness. Add 6 drops of HCl and evaporate to dryness.
- 19 Dissolve the sample in 1 mL of H_2O_2 -HCl solution and load it onto an anion column that has been preconditioned with 2 mL of the H_2O_2 -HCl solution. Rinse the tube with 1 mL of the H_2O_2 -HCl solution and pass it through the column. Wash the column with 2 mL of 8 M HNO_3 . Rinse the tip of the column with deionized water and discard the eluant.
- 20 Elute the plutonium into a clean 10 mL quartz test tube using three 1 mL additions of concentrated HBr. Allow each HBr addition to drain completely before adding the next.
- 21 Slowly evaporate the HBr solution to dryness.
- 22 Add 4 drops of HNO_3 and 4 drops of HClO_4 . Heat at 130° C for one hour. Raise the temperature to 180° C and continue evaporating to dryness. Cool to room temperature and cap the quartz tube.
- 23 Submit the sample for analyses.

Note 1. The initial separation of plutonium is accomplished on an anion exchange column that is prepared by adding 3 mL of resin to a Bio-Rad Poly-Prep chromatography column. The final 2 columns used in this procedure are made from disposable automatic pipette tips, approximately 7 cm long and 5 mm i.d. A plug of prewashed quartz wool is placed in the tip and resin is added to a depth of 2 cm.

Note 2. The eluent from steps 6-8 should be combined and saved if americium analyses are required.

C. REAGENTS

^{242}Pu Tracer (2 ng/mL in 2 M HNO_3 , calibrated to NIST standard 949f)

HClO_4 conc

HNO_3 conc, 8 M, 2 M

HBr 47% (unstabilized)

HI 48% (unstabilized)

HCl conc, 0.5 M

H_2SO_4 0.1 M

Aqua regia 3:1 mixture, by volume, of conc HCl and conc HNO_3

HI-HCl mixture 1:9 mixture, by volume, of 48% HI and conc HCl

$\text{H}_2\text{O}_2\text{-HCl}$ reagent 2 drops of 30% H_2O_2 to 10 mL conc HCl

HF-HCl reagent; 0.06 M HF in conc HCl

Bio-Rad macroporous anion exchange resin AGMP-1, 50 to 100 mesh This resin is pretreated by warming overnight in a mixture of 50% conc HCl and 50% Type 1 reagent grade water It is washed 20 times with Type 1 reagent grade water and stored as an aqueous slurry

Americium Separation Procedure 1

Americium-241 In Environmental Matrices (Less Than 2-Gram Samples)-
Alpha Spectrometry

A INTRODUCTION

This procedure summarizes portions of the americium separation procedure for water samples which was developed by D Knab, R J Peters, and W Eberhardt of the Environmental Measurement Group (EM-9) at Los Alamos National Laboratory (LANL). The complete procedure is Method No ER120, which is titled "Americium-241 In Environmental Matrices (Less Than 2-Gram Samples) - Alpha Spectrometry," and is published in the LANL document LA-10300-M. The americium is separated from matrix material by cation exchange in HCl. It is then separated from most actinides and lanthanides by anion exchange with alcohol-nitric acid solution. The americium is collected by coprecipitation on NdF_3 . The NdF_3 is concentrated on a 25 mm Millipore filter by vacuum filtration. The Millipore filter is mounted on a stainless steel planchet and counted by alpha spectrometry.

B CHEMICAL SEPARATION PROCEDURE

- 1 Place ^{243}Am tracer, an aliquot of the water sample and 10 mL of concentrated HNO_3 in a Pyrex beaker and begin the evaporation process using a hot plate
- 2 Continue adding water to the beaker until a total of 2000 mL of water is evaporated to dryness
- 3 Add 10 mL of concentrated HNO_3 and evaporate the solution to dryness
- 4 Add 10 mL of concentrated HNO_3 and heat to boiling. When the sample begins steaming, **CAREFULLY**, add 6 drops of 48% HF while swirling the sample. Evaporate to dryness.
- 5 Wash down the sides of the beaker with 10 mL of concentrated HNO_3
6. While heating the sample, add 30% H_2O_2 by drops until all organic materials are decomposed.
7. Dissolve the residue in 20 mL of concentrated HNO_3 , carefully washing down the sides of the beaker
8. Add 5 mL of concentrated HCl to the beaker and evaporate to approximately 1 mL. Remove the sample from the hot plate and cool
9. Add 20 mL of 6 M HCl and 1 mL of saturated H_3BO_3 to the sample

10. Evaporate the solution to dryness on low heat using either the sample as dissolved above or the americium fraction collected from the appropriate plutonium anion exchange column
- 11 Add 20 mL of concentrated HCl to dissolve the sample residue, rinsing the sides of the beaker Evaporate to dryness
- 12 Add 20 mL of concentrated HCl to the sample and evaporate to 4 mL While the sample is still warm, dilute to 50 mL with water
- 13 Filter the sample onto the cation exchange column that has been preconditioned with two 20-mL aliquots of 0.5 M HCl (See Note 1)
- 14 Wash the beaker and column with 10 mL of 0.5 M HCl
- 15 Wash the column with four 25-mL aliquots of 2 M HCl Let each addition drain to the resin before adding the next aliquot
- 16 Place a 100 mL beaker under the column and elute the americium with three 25-mL aliquots of 4 M HCl
- 17 Add 5 mL of concentrated HNO₃ to the solution and evaporate until just dry **DO NOT BAKE**
- 18 Add 2 mL of 6 M HNO₃ and 3 mL of ethanol saturated with NaNO₂ Mix and let stand for 1 h
- 19 Pour the sample through the anion exchange column that has been preconditioned with two 20-ml aliquots of fresh 60% ethanol • 40% 6 M HNO₃ (See Note 2)
- 20 Wash the beaker and column with 5 mL of 60% ethanol • 40% 6 M HNO₃
21. Wash the column with two 20-mL aliquots of 75% methanol • 25% 6 M HNO₃
- 22 Wash the column with two 20-mL aliquots of 60% methanol • 40% 6 M HNO₃
- 23 Place a new 100 mL beaker under the column and elute the americium from the column with two 20 mL aliquots of 60% methanol • 40% 2.5 M HNO₃
- 24 Place the beaker on a hot plate and evaporate to dryness **DO NOT BAKE**
- 25 Add 5 mL of concentrated HNO₃ to the beaker and evaporate to dryness **DO NOT BAKE**

- 26 Add 5 mL of 1 M HNO_3 and 50 microliters of neodymium carrier
27. Add 25 microliters of HF to the sample JUST BEFORE filtering through the 25 mm Millipore filter. Process one sample at a time and filter immediately
- 28 Wash the beaker and the filter tower with 5 mL of 1 M HNO_3 • 1 M HF
29. Rinse the tower with 1 mL of 1 M HNO_3 • 1 M HF
- 30 Rinse the tower with two 1-mL aliquots of isopropyl alcohol Turn off the vacuum after the alcohol has passed through and remove the filter
- 31 Mount the filter on a stainless steel planchet and submit for counting

Note 1 All ion exchange columns used in this procedure are 197-mm-long by 7-mm-i d with a 100-mL top reservoir and a tip tapered to 2 mm i d The tips are packed loosely with glass wool The cation exchange resin is AG 50x4, 100-200 mesh resin that is loaded in the column to a height of 17 cm

Note 2 The anion exchange column is prepared by transferring MP-1, 100-200 mesh resin slurry into the tube to a settled height of 9 cm

REAGENTS

243Am tracer
HNO₃ conc, 6 M
HF 48%
H₂O₂ 30%
HCl conc, 4 M, 2 M, 0.5 M
H₃BO₃ saturated
ethanol saturated with NaNO₂
60% ethanol • 40% 6 M HNO₃
75% methanol • 25% 6 M HNO₃
60% methanol • 40% 6 M HNO₃
60% methanol • 40% 2.5 M HNO₃
neodymium carrier 1 mg/mL
1 M HNO₃ • 1 M HF
isopropyl alcohol

Americium Separation Procedure 2

by
D. W. Efur, J. Drake, and G. G. Miller

Separation and Purification of Americium from Waters Containing High Calcium Contents

A INTRODUCTION

We have developed a procedure for analyzing americium from water samples containing high calcium contents. The americium is extracted from 12 M HNO_3 into Dibutyl-N-N-Diethylcarbamoylphosphonate (DDCP) and back-extracted into 6 M HCl . Final purification is accomplished by anion exchange chromatography.

B PROCEDURE

1. Add ^{243}Am tracer, 800 mL of the water sample and 30 mL of 16 M HNO_3 to a 1000 mL glass beaker and begin the evaporation process using a hot plate.
2. Continue adding water to the beaker until a total of 2000 mL of water is evaporated.
3. Add 30 mL of 16 M HNO_3 and evaporate to near dryness, i.e., 0.5-1.5 mL.
4. Dissolve the sample in 50 mL of 8 M HNO_3 .
5. Pass the solution through a large anion exchange column that has been preconditioned with 20 mL of 0.5 M HCl and 20 mL of 8 M HNO_3 . Collect the eluate in a clean 250 mL glass beaker. (See note 1).
6. Rinse the beaker that originally contained the sample with 10 mL of 8 M HNO_3 and pass the rinse through the column.
7. Rinse the column with 10 mL of 8 M HNO_3 .
8. Place the beaker containing the eluate from steps 6-8 on a hot plate and evaporate to dryness.
9. Dissolve the sample in 50 mL of 12 M HNO_3 and transfer the solution to a 125 mL separatory funnel.
10. Add 3 mL of Dibutyl-N-N-Diethylcarbamoylphosphonate (DDCP) and extract for 3 minutes.

Appendix 5

- 11 Allow the separatory funnel to set undisturbed for 1 hour to insure complete phase separation
- 12 Discard the aqueous phase
- 13 Add 10 mL of toluene to the DDCP
- 14 Add 10 mL of 6 M HCl to the separatory funnel and mix vigorously for 1 minute to back-extract the americium. Allow the phases to separate for 5 minutes
- 15 Transfer the aqueous phase containing the americium from the separatory funnel into a clean 60 mL separatory funnel
- 16 Repeat the back extraction two additional times using 10 mL aliquots of 6 M HCl
- 17 Add 10 mL of toluene to the 60 mL separatory funnel containing the 6 M HCl from the 3 back-extractions and mix for 1 minute. Let the layers separate for 5 minutes before discarding the organic layer. Repeat
- 18 Transfer the hydrochloric acid from the separatory funnel into a clean 250 mL glass beaker and evaporate the solution to dryness on a hot plate
- 19 Cool to room temperature and add 10 mL of 16 M HNO₃ and fume to dryness. Repeat 2 times
- 20 Add 10 mL of 16 M HNO₃ and 10 mL of 12 M HClO₄. Fume to dryness
- 21 Dissolve the sample in 4 mL of 12 M HCl. Add 12 mL of acetone and mix thoroughly. Pass the solution through a large anion exchange column that has been conditioned with 15 mL of acetone-hydrochloric acid reagent (See note 2)
- 22 Rinse the beaker with 5 mL of the acetone-hydrochloric acid reagent and pass the rinse through the column.
- 23 Rinse the column with 5 mL of the acetone-hydrochloric acid reagent
- 24 Elute the americium from the column into a clean 30 mL glass beaker with 3 separate 5 mL additions of 10 M HCl
- 25 Evaporate the sample to dryness on a hot plate
- 26 Add 3 mL of 16 M HNO₃ and 1.5 mL of 12 M HClO₄ and evaporate to dryness
- 27 Dissolve the sample in 2 mL of 12 M HCl. Add 6 mL of acetone and mix thoroughly. Pass the solution through a small anion exchange column that has been conditioned with 5 mL of the acetone-hydrochloric acid reagent

- 28 Rinse the beaker with 6 mL of the acetone-hydrochloric acid reagent and pass the rinse through the column
- 29 Rinse the column with 2 mL of the acetone-hydrochloric acid reagent
- 30 Elute the americium from the column into a clean 10 mL quartz test tube with 6 mL of 10 M HCl
- 31 Evaporate the sample to dryness using a hot plate
- 32 Add 1 mL of 16 M HNO₃ and evaporate to dryness
- 33 Add 4 drops of 16 M HNO₃ and 4 drops of 12 M HClO₄. Heat at 130° C for 1 hour. Raise the temperature to 180° C and continue evaporating to dryness. Cool to room temperature and cap the quartz tube
- 34 Submit the sample for mass spectrometric analyses

Note 1 The large column used in this procedure is prepared by adding 3 mL of resin to a Bio-Rad Poly-Prep chromatography column. The small column used in this procedure is made from a disposable automatic pipette tip, approximately 7 cm long and 5 mm i.d. A plug of quartz wool is placed in the tip and resin is added to a depth of 2 cm.

Note 2 The acetone-hydrochloric acid reagent must be prepared immediately before use.

C REAGENTS

²⁴³Am Tracer. 9.1×10^{10} atoms ²⁴³Am in 2 M HCl, standardized on alpha spectrometers whose operational characteristics have been determined by measuring NIST certified standards

Bio-Rad macroporous anion exchange resin AGMP-1, 50 to 100 mesh. The resin is pretreated by warming overnight in a mixture of 50% 12 M HCl and 50% Type 1 reagent grade water. It is washed 20 times with Type 1 reagent grade water and stored as an aqueous slurry.

Acetone-hydrochloric acid reagent Mix 1:3 (v/v) 12 M HCl and acetone
Dibutyl-N,N-Diethylcarbamoylphosphonate (DDCP)

Toluene

HClO₄ 12 M

HNO₃ 16 M, 12 M, 8 M

HCl 12 M, 10 M, 6 M, 0.5 M

Appendix 6

Mass Spectrometric Measurement of Plutonium from Rocky Flats Water Samples

A. Introduction

This procedure describes the instrument calibration, quality assurance tests, sample mounting techniques, instrument operation parameters and calculations required to measure the ^{239}Pu and ^{240}Pu in Rocky Flats water samples

The operations required to achieve the actual measurement of plutonium include all of the above elements. They must be performed sequentially, and they are discussed in the order in which they must be performed

B. Instrument Calibration

There are two instrumental parameters which must be determined prior to analyzing any sample. These are determination of system dead time and determination of isotope fractionation

B1. System Dead Time

For any pulse counting detector system there is a finite recovery time for the pulse amplifier after a pulse is amplified. Any ion which arrives at the detector during this recovery period will not be detected. This recovery period is commonly referred to as "dead time". A correction must be made for the dead time for all ion counting data. This correction is calculated by Equation 1

Equation 1

$$N_t = \left(\frac{1}{1 - (N_m \cdot t)} \right) \cdot N_m$$

where N_m = measured count rate (counts/second)
 N_t = true count rate (counts/second)
 t = system deadtime in seconds

The value for t may be measured electronically or by the use of appropriate isotopic standards. The dead time which is determined by electronic means is only valid if the dead time of the pulse amplifier and counter are significantly greater than the dead time of the electron multiplier or photon conversion system (e.g. Daley Detector) used to detect the incoming ion. For this reason it is recommended that the dead time always be measured both electronically and by appropriate standards

The electronic determination of the dead time may be accomplished in the following manner. A high speed double pulse generator is attached to the input of the pulse amplifier. The amplitude of the pulse is adjusted to match the mean amplitude of the output of the ion detector (electron multiplier or photon converter) as previously determined by a pulse height distribution measurement. The pulse width is adjusted to mimic the mean pulse width of the ion detector. The count rate is adjusted to a level of 50,000 - 100,000 counts as registered on the counter in the system. The double pulse separation time is then varied until the number of pulses is either halved or doubled. The pulse separation at which this transition occurs is the dead time of the pulse amplifier-counter system under test. For a properly functioning system this transition should be quite sharp (less than 0.5 nanosecond) and reproducible when approached from either direction.

There are two methods in which isotopic standards may be utilized for the determination of system dead time. The CBNM 072 series of uranium standards provide a very simple means of determining system dead time because in each standard the $^{235}\text{U}/^{238}\text{U}$ ratio is quite close to 1. In this condition the dead time correction for each isotope is identical and may be ignored. This permits the use of the measured $^{235}\text{U}/^{238}\text{U}$ ratio for calculation of the isotopic fractionation correction factor by Equation 2.

Equation 2

$$R_{N3} = \frac{1}{\left[\left(\frac{5}{3} \left[\frac{R_{M5}}{R_{C5}} \right] - 1 \right) + 1 \right]}$$

where:

- R_{M5} = measured $^{235}\text{U}/^{238}\text{U}$
- R_{C5} = certified $^{235}\text{U}/^{238}\text{U}$
- R_{M3} = measured $^{233}\text{U}/^{238}\text{U}$
- R_{N3} = $^{233}\text{U}/^{235}\text{U}$ corrected for fractionation

In the CBNM 072 uranium reference material series the ^{233}U abundance is decreased for each increase in standard designation. The CBNM 072-4 AND CBNM 072-5 reference materials have certified $^{235}\text{U}/^{238}\text{U}$ ratios of 0.29763 and 0.099313 respectively. These standards provide the most accurate measurement of dead time because they provide a sufficiently large differential count rate between the ^{233}U and the ^{238}U peak intensities while still providing an adequate ^{233}U intensity for precise counting statistics. Table I provides an easily interpreted data presentation which demonstrates the relationships between count rate and dead time. It may be seen that doubling either the count rate or the dead time will lead to the same correction. For example, the correc-

tion for 200,000 cps at 10 nanoseconds is the same as the correction for 100,000 cps at 20 nanoseconds. Also, if one measures one peak at 100,000 cps and a second peak at 200,000 cps, the net correction to the ratio is that calculated for a 100,000 cps peak. The dead time correction is, therefore, a function of the differential count rate between two peak intensities. This forms the basis of the equation for calculating dead time from measured data.

Equation 3

$$E_t = \frac{R_{C3}}{R_{N3}}$$

where E_t = error due to dead time
 R_{C3} = certified $^{233}\text{U}/^{238}\text{U}$
 R_{N3} = $^{233}\text{U}/^{238}\text{U}$ corrected for fractionation (Equation 2)

Equation 4

$$t = \frac{1 - \frac{N_M}{E_t}}{N_M - R_{N3}N_M}$$

where t = dead time correction
 E_t = error due to dead time (Equation 3)
 R_{N3} = $^{233}\text{U}/^{238}\text{U}$ corrected for fractionation (Equation 2)
 N_M = ^{238}U count rate when R_{N3} is measured

There is an alternate method of calculating dead time which does not require an exact certified ratio. The method also provides a check against isotopic contamination of the standard used in the method just described. In this second method it is necessary to measure the same sample at high count rate (greater than 300,000 cps) and a low count rate (~ 100,000 cps). Reference Material CBNM 072-3 provides the best ratio set for this procedure because the ^{233}U peak intensity is still high enough for precise measurement at the 100,000 CPS ^{238}U intensity.

In this method the measured $^{235}\text{U}/^{238}\text{U}$ ratio taken at 300,000 CPS is taken as the true ratio for calculation of fractionation correction for the low intensity measurement. It, therefore, becomes R_{C3} in Equation 2. R_{M3} at high intensity becomes R_{C3} in Equation 3 and R_{N3} is calculated for the low intensity measurement for use in both Equation 3 and Equation 4.

In Equation 4 the differential count rate ratio which is shown as $N_M - 4N_3N_M$ is not used. Instead the term $N_H - N_M$ is substituted and Equation 4 is written as Equation 5.

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Equation 5

$$t = \frac{1 - \frac{1}{E_1}}{N_H - N_L}$$

where N_H = the mean count rate at which the $^{233}\text{U}/^{238}\text{U}$ ratio was taken for the high intensity data set

and N_L = the mean count rate at which the $^{233}\text{U}/^{238}\text{U}$ ratio was taken for the low intensity data set

This method of calculating dead time has the advantage that it yields a correct dead time value even if a contamination is present for one of the certified values. It has the disadvantage that small errors in measuring any of the four ratios will cause a larger error in the measured dead time (t).

In practice the dead times measured electronically and by both of the ratio based methods should yield values with ± 1 nanosecond. If significant differences are observed, a fault must be expected in either the detector, amplifier, counter system or in the purity of the standards used. These faults should be identified and corrected before proceeding with other measurements.

Table I

t	100,000CPS	200,000CPS	300,000CPS
1.0×10^{-8}	1.00102	1.00200	1.00301
1.1×10^{-8}	1.00110	1.00220	1.00331
1.2×10^{-8}	1.00120	1.00240	1.00361
1.3×10^{-8}	1.00130	1.00260	1.00391
1.4×10^{-8}	1.00140	1.00280	1.00422
1.5×10^{-8}	1.00150	1.00300	1.00452
2.0×10^{-8}	1.00200	1.00402	1.00603
3.0×10^{-8}	1.00300	1.00603	1.00908
4.0×10^{-8}	1.00400	1.00806	1.01215

B. ISOTOPE FRACTIONATION FACTOR

For any thermal ionization process there are physical processes which cause isotopic fractionation to occur during ion formation. These processes can include (a) small differences in isotopic evaporation ratios, (b) small differences in the dissociation rates of molecular species, (c) small differences in migration rates through a semifluid system (e.g. platinum overplate or glass bead). All of these processes tend to favor preferential ionization of the lightest mass early and the heavy mass late in the ionization process. All of these processes are affected by heating rates, final filament temper-

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ature, sample composition in the region (both elemental purity and molecular species) and gas composition in the region near the ionization surface. Because these conditions are difficult to reproduce it has been observed that the most accurate results are achieved by analyzing Reference Materials which have been subjected to at least the final stage cleaning chemistry and analyzed independently by each analyst. Thus fractionation factors can be process, analyst, instrument and heating protocol specific.

Fractionation corrections are determined by repeated analysis of RMs with well certified ratios using controlled and repeatable sample mounting procedures, followed by the use of well controlled instrumental pump down and filament heating protocols. Standards having the widest possible isotopic spread between the certified masses are chosen. The ratio chosen should, if possible, be as close to 1:1 as can be obtained. Thus, a sample of 1:1 ^{235}U to ^{238}U or a sample of 1:10 ^{233}U to ^{238}U .

For purposes of calculation, the measured ratio corrected for deadtime is divided by the certified ratio. For simplicity the $^{233}/^{238}$ ratio is preferred to the $^{238}/^{233}$ since this will yield a number greater than 1.

$${}^7F_5 = R_M/R_C \text{ where } \begin{array}{l} R_M = \text{measured } ^{233}\text{U}/^{238}\text{U} \\ R_C = \text{certified } ^{233}\text{U}/^{238}\text{U} \end{array}$$

$${}^7F_1 = (R_M/R_C - 1)/5 \quad (\text{this assumes a linear mass dependence})$$

If one arbitrarily assigns a value of 1.0000 to the lowest mass M_x measured then the fractionation correction for any other mass ($M_x + Y$) is

$${}^7F_{(X+Y)} = (Y \times {}^7F_1) + 1$$

In this formulation Y is equal to the integral mass difference between M_x with ${}^7F_x = 1$ and the mass ($X + Y$) for which ${}^7F_{(X+Y)}$ is being calculated.

All of the 7F_1 factors for a given operator, instrument and procedure combination are stored in the fractionation factor file. Therefore, calculation of the corrected ion beam intensity is simply:

$${}^7I_{TX} = {}^6I_{TX} \times {}^7F_X$$

Note: The fractionation factors for a given procedure must be re-evaluated when a change is made in chemical separation, filament loading, or filament heating parameters. Changes in vacuum quality within the ion source housing may also cause unacceptable alteration of the fractionation correction.

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C. Quality Assurance Tests

The primary source of error for environmental measurements is uncontrolled contamination from external sources. A series of tests are routinely performed to evaluate the adequacy of the procedures to control the blank. These tests are described below.

Spike Characterization

Isotopically pure spikes are a fundamental requirement both for blank evaluation and determination of the total plutonium in the sample. An appropriate dilution of each spike is prepared by dilution in 2M HCl. The isotopic purity of the spike is determined by repeated measurement of 1 nanogram quantities on the mass spectrometer. For this program the $^{239}\text{Pu}/^{242}\text{Pu}$ and the $^{239}\text{Pu}/^{244}\text{Pu}$ ratios of the spike are less than 1 ppm and the measurement must be performed on a two stage mass spectrometer. After the isotopic purity of the spike has been determined, the concentration of each spike (in atoms/gram of solution) is determined from prepared mixes with solutions of NBS 949f metal. This standard is high purity metal certified for both elemental and isotopic content. A minimum of two weighed metal pieces is dissolved and diluted gravimetrically to provide solutions of known concentrations. At least two weighed mixes of each spike and each aliquot of NBS 949f are prepared for each calibration.

Blank Evaluation

All reagents utilized for the preparation of spikes, for chemical separations and for sample mounting are prepared in quantities adequate for approximately 12 months of operation. These master solutions are double bagged and stored in class 100 clean air conditions. Small portions are transferred to small, clean, containers as working solutions and for reagent characterization tests. Prior to initiation of any analytical procedures with a batch of new reagents, the reagents are tested for plutonium contamination by spiking an appropriate quantity (approximately 10 times the quantity to be used in the process) with a weighed quantity of spike. The solution is evaporated to dryness, mounted by our standard procedure, and mass spectrometrically analyzed for isotopic content. The quantity of any isotope in the test sample can be calculated by the following isotope dilution equations:

$$\text{ATOMS OF } ^x\text{Pu}_B = ^x\text{Pu}_m / ^s\text{Pu}_m \times N_s - ^x\text{Pu}_s / ^s\text{Pu}_s \times N_s$$

Where $^x\text{Pu}_B$ = atoms of isotope x in the blank

$^x\text{Pu}_m / ^s\text{Pu}_m$ = measured ratio of isotope x and s in the mix

$^x\text{Pu}_s / ^s\text{Pu}_s$ = measured ratio of isotope x and s in spike

^sPu = spike isotope either ^{242}Pu or ^{244}Pu

N_s = atoms of spike isotope s added to the mix

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A continuing evaluation of the plutonium blank is conducted by performance of two additional tests. These are the loading blank and the process blank

Loading Blank — The loading blank tests the quality of all reagents used to mount the sample for mass spectrometric analysis. One nanogram of ^{242}Pu spike is electrodeposited using our standard sample mounting procedure and analyzed mass spectrometrically. If reagent contamination is detected, the reagents are replaced and the loading blank is repeated until reagent purity is restored

Process Blank — An aliquot of type 1 reagent grade water is spiked and processed through the entire separation scheme in parallel with each sample batch. The process blank must be no more than 10% of the desired detection limit. If contamination of the process blank is observed, the entire group of samples prepared with that blank must be rejected and new aliquots reprocessed

D. Sample Mounting Procedure

The mounting of the previously purified plutonium is accomplished by electrodeposition of the plutonium with a small quantity of platinum. A larger quantity of platinum is then electrodeposited over the plutonium to provide a diffusion barrier which dissociates plutonium molecular species and provides high ionization efficiency

Reagents for the sample mounting procedure include

- 1 1.5 M HCl for dissolution of the purified sample
- 2 1.5 M NH_4Cl buffered to pH 2-7
- 3 Platinum DNS. This is a proprietary solution supplied by Johnson Matthey Corporation. The .01 g/ml platinum concentration in the solution is diluted to 5mg/ml with 1.5 M HCl for this process

The pH adjustment of the NH_4Cl is accomplished by bubbling pure ammonia through 1.5 M HCl. The use of ammonium hydroxide is not recommended due to the presence of traces of colloidal silica which significantly reduce electrodeposition efficiency

Detailed Sample Mounting Procedure

1. Assemble the electrodeposition apparatus
2. Pipette 100 μl of 1.5 M NH_4Cl and 10 μl of 1.5 M HCl into the 13 x 100 mm quartz tube containing the purified plutonium sample
3. Warm the solution under a heat lamp for 2 minutes
4. Transfer the solution to the filament on the electrodeposition apparatus
5. Electrolyze for 30 minutes at 3.5V.
6. Reduce the plating voltage to 3V and add 5 μl of platinum DNS solution (25 μg of Pt)

7. Electrolyze for 20 minutes at 3V
8. With the plating voltage at 3V rinse the electrolyte from the filament with deionized water.
9. Remove the filament from the plating apparatus and rinse thoroughly with deionized water and then with acetone that has been distilled in glass
10. Dry the filament at 350°C under a heatlamp (This will require a filament current of 1.25 amps for 5 minutes)
11. Place the filament into the filament carrier for insertion into the mass spectrometer

E. Mass Spectrometric Analysis

The heating pattern for analysis of plutonium has been experimentally determined to provide maximum stability and the most reproducible fractionation with a loading of 1 nanogram ($\sim 2.3 \times 10^{12}$ atoms) The heating pattern is shown in Table II

**Table II —
Optimized Heating Pattern for Pu**

Time (min)	Filament Temp. C.*
0	1000
2	1100
4	1200
6	1300 Begin search
8	1350 Optimize ion source
10	1400 Tuning
12	1450 Start base line
20	1450 acquisition on
30	1450 bases of interest
60	1450 Data acquisition should be complete

*Filament temperatures measured by 2 color pyrometer

2. Baseline Measurement
Baselines are taken at half masses 238.5, 239.5 and 241.5
3. Data Acquisition
Collect at least 4 sets of ratios for $^{239}\text{Pu}/^{242}\text{Pu}$
4. Take baselines at 239.5, 240.5 and 241.5
Collect at least 4 sets of ratios for $^{240}\text{Pu}/^{242}\text{Pu}$
5. The mass spectrometer computer readout will provide the mean $^{239}\text{Pu}/^{242}\text{Pu}$ and $^{240}\text{Pu}/^{242}\text{Pu}$ ratios corrected for dead time and fractionation

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6. Calculate total atoms of spike added from equation 6
7. Calculate the total atoms of ^{239}Pu and ^{242}Pu from equations 7 and 8
- 8 Calculate concentration of ^{239}Pu and ^{240}Pu using equation 9
- 9 Calculate pCi ^{239}Pu from equation 10
- 10 Calculate pCi ^{240}Pu from equation 11.

Equation 6

$$N_S = WT_X \times C_S$$

where N_S = Number of atoms of the spike isotope added to the sample
 WT_S = Wt of spike solution added
 C_S = Atoms of spike isotope per gram of spike solution

Equation 7

$$N_{239} = (R_{9M} \times N_S) - (R_{9S} \times NS)$$

where N_{239} = Atoms of ^{239}Pu in sample
 R_{9M} = Measured $^{239}\text{Pu}/^{242}\text{Pu}$ in mix
 R_{9S} = $^{239}\text{Pu}/^{242}\text{Pu}$ in spike

Equation 8

$$N_{240} = (R_{4M} \times N_S) - R_{4S} \times N_S$$

where N_{240} = Atoms of ^{240}Pu in sample
 R_{4M} = Measured $^{240}\text{Pu}/^{242}\text{Pu}$ in mix
 R_{4S} = $^{240}\text{Pu}/^{242}\text{Pu}$ in spike

Equation 9:

$$C_x = N_x / \text{Sample wt.}$$

where C_x = Concentration of isotope x
 N_x = Atoms of isotope x in sample

Equation 10:

$$\text{pCi/g } ^{239}\text{Pu} = C_9 / 4.0606 \times 10^{10}$$

Equation 11:

$$\text{pCi/g } ^{240}\text{Pu} = C_0 / 1.1048 \times 10^{10}$$

Appendix 7

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	P O N D	R F SAMPLE #	SAMPLE SIZE COLLECTED LITERS	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L	COMMENT
08-28-91	A 4 2 3	C2	SW60152WC	9 5	2	0 0436	monthly
09-09-91	A 4 2 3	C2	SW60159WC	9 5	2	0 0396	monthly
10-14-91	A 4 2 3	C2	SW60163WC	9 5	2	0 0475	monthly
11-11-91	A 4 2 3	C2	SW60169WC	9 5	2	0 0304	monthly
12-12-91	A 4 2 3	C2	SW60189WC	9 5	2	0 0209	monthly
12-13-91	3 4 1 1*	C2	SW60190WC	9 5	2	0 0196	*
01-16-92	A 4 2 3	C2	SW60200WC	9 5	2	0 0126	monthly
02-19-92	A 4 2 3	C2	SW60213WC	3 8	2	0 0202	monthly
03-18-92	A 4 2 3	C2	SW60220WC	3 8	2	0 0433	monthly
04-20-92	A 4 2 3	C2	SW60224WC	3 8	2	0 0510	monthly
05-13-92	A 4 2 3	C2	SW60232WC	3 8	2	0 0966	monthly
06-16-92	A 4 2 3	C2	SW60236WC	3 8	2	0 0623	monthly
07-22-92	A 4 2 3	C2	SW60246WC	3 8	2	0 0799	monthly
08-11-92	A 4 2 3	C2	SW60249WC	3 8	2	0 0342	monthly
09-14-92	A 4 2 3	C2	SW60265WC	3 8	2	0 0684	monthly

These are the plutonium results for the monthly sampling of pond C2

* Special Analyses of C Pond Water for Polzer and Essington Study

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	POND	R F SAMPLE #	SAMPLE SIZE COLLECTED LITERS	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L	COMMENT
08-27-91	A 4 2 3	STP EFF	SW60155WC	9 5	2	0 0013	monthly
09-09-91	A 4 2 3	STP EFF	SW60162WC	9 5	2	0 0007	monthly
10-15-91	A 4 2 3	STP EFF	SW60166WC	9 5	2	0 0027	monthly
11-11-91	A 4 2 3	STP EFF	SW60170WC	9 5	2	0 0008	monthly
12-17-91	A 4 2 3	STP EFF	SW60196WC	9 5	2	0 0015	monthly
01-06-92	A 4 2 3	STP EFF	SW60199WC	9 5	2	0 0036	monthly
02-26-92	A 4 2 3	STP EFF	SW60206WC	3 8	2	0 0013	monthly
03-25-92	A 4 2 3	STP EFF	SW60221WC	3 8	2	0 0025	monthly
04-21-92	A 4 2 3	STP EFF	SW60225WC	3 8	2	0 0005	monthly
05-13-92	A 4 2 3	STP EFF	SW60233WC	3 8	2	* LIA	monthly
05-13-92	A 4 2 3	STP EFF	SW60233WC	3 8	2	**0 0018	monthly
06-25-92	A 4 2 3	STP EFF	SW60237WC	3 8	2	0 0035	monthly
07-22-92	A 4 2 3	STP EFF	SW60247WC	3 8	2	0 0027	monthly
08-12-92	A 4 2 3	STP EFF	SW60259WC	3 8	2	0 0012	monthly
09-14-92	A 4 2 3	STP EFF	SW60263WC	3 8	2	0 0011	monthly

These are the plutonium results for the monthly sampling of the effluent from the water treatment plant

* LIA = Sample lost in analyses

** This sample was traced with ^{243}Am The plutonium value reported has been corrected for the ^{239}Pu contribution from the ^{243}Am tracer ^{239}Pu is the alpha decay product of ^{243}Am

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	P O N D	R F SAMPLE #	SAMPLE SIZE COLLECTED LITERS	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L	COMMENT
08-27-91	A 4 2 3	A4	SW60154WC	9 5	2	0 0024	monthly
09-19-91	A 4 2 3	A4	SW60161WC	9 5	2	0 0011	monthly
10-15-91	A 4 2 3	A4	SW60165WC	9 5	2	0 0012	monthly
11-11-91	A 4 2 3	A4	SW60167WC	9 5	2	0 0041	monthly
12-17-91	A 4 2 3	A4	SW60195WC	9 5	2	0 0009	monthly
01-08-92	A 4 2 3	A4	SW60201WC	9 5	2	0 0023	monthly
02-20-92	A 4 2 3	A4	SW60212WC	3 8	2	0 0016	monthly
03-17-92	A 4 2 3	A4	SW60207WC	3 8	2	0 0199	monthly
04-20-92	A 4 2 3	A4	SW60222WC	3 8	2	0 0029	monthly
05-13-92	A 4 2 3	A4	SW60230WC	3 8	2	0 0041	monthly
06-16-92	A 4 2 3	A4	SW60234WC	3 8	2	0 0059	monthly
07-22-92	A 4 2 3	A4	SW60244WC	3 8	2	0 0026	monthly
08-11-92	A 4 2 3	A4	SW60250WC	3 8	2	0 0025	monthly
09-15-92	A 4 2 3	A4	SW60264WC	3 8	2	0 0022	monthly

These are the plutonium results for the monthly sampling of pond A4

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Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	POND	R F SAMPLE #	SAMPLE SIZE COLLECTED LITERS	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L	COMMENT
08-27-91	A 4 2 3	B5	SW60153WC	9 5	2	0 0053	monthly
09-09-91	A 4 2 3	B5	SW60160WC	9 5	2	0 0026	monthly
10-14-91	A 4 2 3	B5	SW60164WC	9 5	2	0 0032	monthly
11-11-91	A 4 2 3	B5	SW60168WC	9 5	2	0 0055	monthly
12-17-91	A 4 2 3	B5	SW60197WC	9 5	2	0 0038	monthly
01-06-92	A 4 2 3	B5	SW60198WC	9 5	2	0 0082	monthly
02-20-92	A 4 2 3	B5	SW60218WC	3 8	2	0 0067	monthly
03-18-92	A 4 2 3	B5	SW60219WC	3 8	2	0 0243	monthly
04-20-92	A 4 2 3	B5	SW60223WC	3 8	2	0 0036	monthly
05-13-92	A 4 2 3	B5	SW60231WC	3 8	2	0 0040	monthly
06-16-92	A 4 2 3	B5	SW60235WC	3 8	2	0 0077	monthly
06-16-92	A 4 2 3	B5	SW60235WC-F	3 8	2	0 0100	monthly
07-22-92	A 4 2 3	B5	SW60245WC	3 8	2	0 0022	monthly
08-12-92	A 4 2 3	B5	SW60254WC	3 8	2	0 0053	monthly
09-14-92	A 4 2 3	B5	SW60266WC	3 8	2	0 0046	monthly

These are the plutonium results for the monthly sampling of pond B5

Appendix 7

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	P O N D	R F SAMPLE #	SAMPLE SIZE COLLECTED LITERS	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L	COMMENT
02-03-92	A 4 2 5	C2	SW70245WC	9 5	2	0 0095	Filter Sample
02-03-92	A 4 2 5	C2	SW70246WC	9 5	2	0 0103	Filter Sample
02-03-92	A 4 2 5	C2	SW70249WC	9 5	2	0 0076	Filter Sample
02-03-92	A 4 2 5	C2	SW70251WC	9 5	2	0 0116	Filter Sample
02-03-92	A 4 2 5	C2	SW70252WC	9 5	2	0 0050	Filter Sample
02-03-92	A 4 2 5	C2	SW70244WC	9 5	2	0 0135	Filter Sample
02-03-92	A 4 2 5	C2	SW70248WC	9 5	2	0 0110	Filter Sample

These were a series of special samples that were filtered at RFP as part of their remediation studies. The plutonium concentrations reported above are the concentrations in the water after filtration.

Appendix 7

Mass Spectrometric Measurements of Plutonium

SEPARATION TIME	TASK #	POND	R F SAMPLE #	TEST SAMPLE SIZE (Liters)	MEASURED VALUE* ^{239}Pu ATOMS/L	MEASURED VALUE* ^{244}Pu ATOMS/L	COMMENT
01-07-92	A 4 3 1	C2	SW60179WC	2	1.35×10^9	2.17×10^9	STABILITY STUDY
01-24-92	A 4 3 1	C2	SW60179WC	2	1.30×10^9	1.97×10^9	STABILITY STUDY
03-31-92	A 4 3 1	C2	SW60179WC	2	1.23×10^9	2.03×10^9	STABILITY STUDY
01-07-92	A 4 3 1	C2	SW60180WC	2	1.78×10^9	2.12×10^9	STABILITY STUDY
01-24-92	A 4 3 1	C2	SW60180WC	2	1.42×10^9	2.33×10^9	STABILITY STUDY
03-31-92	A 4 3 1	C2	SW60180WC	2	1.36×10^9	2.16×10^9	STABILITY STUDY
01-07-92	A 4 3 1	C2	SW60181WC	2	1.32×10^9	2.02×10^9	STABILITY STUDY
01-24-92	A 4 3 1	C2	SW60181WC	2	1.23×10^9	2.07×10^9	STABILITY STUDY
03-31-92	A 4 3 1	C2	SW60181WC	2	1.57×10^9	2.19×10^9	STABILITY STUDY

These samples of Pond C2 water were traced with ^{244}Pu to study long-term stability of samples in storage. Plutonium values are reported in atoms instead of pCi/L.

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Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	P I ID #	SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L	COMMENT
08-27-91	A 4 2 3	PB10401	2	0004	Process Blank
09-10-91	A 4 2 3	PB10402	2	0005	Process Blank
10-11-91	A 4 2 3	PB	2	0003	Process Blank
11-11-91	A 4 2 3	PB10403	2	0001	Process Blank
12-19-91	A 4 2 3	PB	2	0004	Process Blank
01-21-92	A 4 2 3	PB10405	2	0005	Process Blank
02-06-92	A 4 2 3	PB10406	2	0004	Process Blank
02-26-92	A 4 2 3	PB10602	2	< 0001	Process Blank
03-12-92	A 4 2 3	PB10409	2	0008	Process Blank
03-26-92	A 4 2 3	PB10411	2	0001	Process Blank
04-12-92	A 4 2 3	PB	2	0010	Process Blank
04-27-92	A 4 2 3	PB10604	2	0002	Process Blank
04-27-92	A 4 2 3	PB10413	2	0002	Process Blank
06-25-92	A 4 2 3	PB10418	2	0007	Process Blank
07-31-92	A 4 2 3	PB10420	2	0002	Process Blank
10-02-91	A 4 2 3	LB	N/A	< 0001	Loading Blank
11-08-91	A 4 2 3	LB	N/A	< 0001	Loading Blank
12-10-91	A 4 2 3	LB	N/A	< 0001	Loading Blank
01-09-92	A 4 2 3	LB	N/A	< 0001	Loading Blank
01-14-92	A 4 4 3	LB	N/A	< 0001	Loading Blank

These are the results for the TIMS loading blank and the reagent blanks that were run concurrently with the monthly pond water samples

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	LANL SAMPLE #	TEST SAMPLE SIZE (Liters)	MEASURED VALUE pCi Pu/g of ²⁴³ Am tracer*
06-23-92	A 4 4 2	2431	0 001	0 0040
06-23-92	A 4 4 2	2432	0 005	0 0027
06-23-92	A 4 4 2	2433	0 010	0 0027

These samples are aliquots of the ²⁴³Am tracer that were analyzed to determine the ²³⁹Pu concentration in the ²⁴³Am tracer that was prepared for use as an isotope dilution tracer for determining the americium content of the ponds at RFP. The values reported in this table are the concentrations of plutonium in the americium tracer.

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	POND	RF SAMPLE #	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi Pu/L*	COMMENT
04-20-92	A 4 4 2	A4	SW60222WC	2	0 0050	
04-20-92	A 4 4 2	B5	SW60223WC	2	0 0057	
04-20-92	A 4 4 2	C2	SW60224WC	2	0 0521	
04-20-92	A 4 4 2	STPEFF	SW60225WC	2	0 0060	
06-05-92	A 4 4 2	N/A	N/A	2	0 0037	Process Blank
05-13-92	A 4 4 2	B5	SW60231WC	2	0 0084	
05-13-92	A 4 4 2	C2	SW60232WC	2	0 1010	
05-13-92	A 4 4 2	STPEFF	SW60233WC	2	0 0045	
06-10-92	A 4 4 2	N/A	N/A	2	0 0041	Process Blank

* These samples were traced with ^{243}Am . The plutonium values represent the original plutonium content of the sample plus the plutonium content of the ^{243}Am tracer. These samples were analyzed as part of the development project designed to decrease the time required to obtain americium analyses.

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Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	P O N D	LANL SAMPLE #	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L*	COMMENT
12-13-91	A4 3 1	C2	RC2-1 R450	10 45	0 0707	Analyzed for Task B
12-13-91	A4 3 1	C2	RC2-1 R2	8 32	0 0202	Analyzed for Task B
12-13-91	A4 3 1	C2	BL-5 F2-1	11 90	5 1E-5	Analyzed for Task B
12-13-91	A4 3 1	C2	BL-5 F10	11 90	5 6E-5	Analyzed for Task B
12-13-91	A4 3 1	C2	BL-5 R450	10 74	0 0004	Analyzed for Task B
12-13-91	A4 3 1	C2	RC2-2 F2-3	10 87	0 0032	Analyzed for Task B
12-13-91	A4 3 1	C2	RC2-2 R2	8 58	0 0111	Analyzed for Task B
12-13-91	A4 3 1	C2	RC2-1 CW	6 38	0 0020	Analyzed for Task B
12-13-91	A4 3 1	C2	RC2-1 F2-10	10 61	0 0043	Analyzed for Task B
12-13-91	A4 3 1	N/A	3 3- SW60194WC-1	11 13	0 0001**	Analyzed for Task B
12-13-91	A4 3 1	C2	RC2-1 F2-2	10 49	0 0037	Analyzed for Task B
12-13-91	A4 3 1	C2	RC2-4 F10	8 49	0 0179	Analyzed for Task B
12-13-91	A4 3 1	C2	RC2-1 F10***		N/A	Analyzed for Task B
12-13-91	A4 3 1	C2	RC2-1 F2-3****		N/A	Analyzed for Task B
12-13-91	A4 3 1	C2	BL-5 F2-3	11 21	5 3E-5	Analyzed for Task B
12-13-91	A4 3 1	C2	BL-5 F2-9	10 90	2 4E-5	Analyzed for Task B
12-13-91	A4 3 1	C2	BL-5 R2 +BL5 2BW&FW	14 48	0 0002	Analyzed for Task B
12-13-91	A4 3 1	C2	RC2-2 R450 +RC2- 2 R450FW	13 41	0 1270	Analyzed for Task B

These samples were analyzed in support of Task B

* Samples have been through treatment for Polzer and Essington's speciation studies. The pCi/L values reported in this table are the amount of activity detected in the treated waters which have been concentrated. The values are not the original plutonium contents of the pond C2 water samples.

** This sample was a field blank consisting of deionized water. It was processed in the field using the same techniques used to collect the water samples analyzed in the speciation study.

*** Sample RC2-1.F10 was lost in analyses. It was replaced by sample RC2-4 F10.

**** Sample RC2-1.F2-3 was lost in analyses. It was replaced by sample RC2-1 F2-2.

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	LANL SAMPLE #	SAMPLE SIZE COLLECTED LITERS	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L*	COMMENT
02-26-92	A4 3 1	RB10602	9 00	9 00	0 00003	Analyzed for Task B
03-18-92	A4 3 1	RB10603	9 00	9 00	0 00002	Analyzed for Task B
04-27-92	A4 3 1	RB10604	9 00	9 00	0 00002	Analyzed for Task B

These samples were analyzed in support of Task B

* These are 9L deionized water samples that were run as processing blanks for the Polzer and Essington speciation studies

Appendix 7

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	P O N D	LANL SAMPLE #	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi*	COMMENT
01-21-92	A4 3 1	C2	RC2-1 R10	N/A	0 2060	Analyzed for Task B
01-21-92	A4 3 1-	C2	RC2-2 R10	N/A	0 0714	Analyzed for Task B
01-21-92	A4 3 1	C2	BL-5 R10	N/A	0 0016	Analyzed for Task B

These samples were analyzed in support of Task B

*These samples were filters submitted by Polzer and Essington. The activity reported above is the total amount of plutonium detected on the filter.

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	P O N D	R F SAMPLE #	SAMPLE SIZE COLLECTED LITERS	P I D #	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L
12-13-91	4 3 2	C2	SW601193WC	227	2-310	0 05	192 3
12-13-91	4 3 2	C2	SW601193WC	227	3-311	0 05	3 0171
12-13-91	4 3 2	C2	SW601193WC	227	3-312	0 05	3 2115
12-13-91	4 3 2	C2	SW601193WC	227	2-291	0 07	0 7516
12-13-91	4 3 2	C2	SW601193WC	227	3-294	0 5	0 0179
12-13-91	4 3 2	C2	SW601193WC	227	2-301	0 1	2 9858
12-13-91	4 3 2	C2	SW601193WC	227	3-204	0 5	0 9039
12-13-91	4 3 2	C2	SW601193WC	227	2 303	0 1	1 0642
12-13-91	4 3 2	C2	SW601193WC	227	3-206	0 5	0 2170
12-13-91	4 3 2	C2	SW601193WC	227	2-313	0 05	994 9
12-13-91	4 3 2	C2	SW601193WC	227	3-314	0 05	548 4
12-13-91	4 3 2	C2	SW601193WC	227	3-315A	0 05	336 9
12-13-91	4 3 2	C2	SW601193WC	227	3-315B	0 05	121 4
12-13-91	4 3 2	C2	SW601193WC	227	2-293	0 07	0 3390

These samples were traced with plutonium and processed in support of Task C

The plutonium concentrations reported in this table are the amounts of plutonium remaining after treatment. They are not the amounts of plutonium originally in the C2 pond water samples.

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	P O N D	R F SAMPLE #	SAMPLE SIZE COLLECTED LITERS	P I ID #	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L
12-13-91	4 3 2	C2	SW601193WC	227	3-296	0 5	0 0120
12-13-91	4 3 2	C2	SW601193WC	227	RB10409	1 0	0 0005
12-13-91	4 3 2	C2	SW601193WC	227	2-320-2	1 0	0 0122
12-13-91	4 3 2	C2	SW601193WC	227	2-320-1	1 0	0 0158
12-13-91	4 3 2	C2	SW601193WC	227	3 320-2	1 0	0 0093
12-13-91	4 3 2	C2	SW601193WC	227	4-320-2	1 0	0 0334
12-13-91	4 3 2	C2	SW601193WC	227	6 320-2	1 0	0 0451
12-13-91	4 3 2	C2	SW601193WC	227	3-320-1	1 0	0 0035
12-13-91	4 3 2	C2	SW601193WC	227	4-320-1	1 0	0 0114
12-13-91	4 3 2	C2	SW601193WC	227	6-320-1	1 0	0 0137
12-13-91	4 3 2	C2	SW601193WC	227	7-320-1	1 0	0 0101
12-13-91	4 3 2	C2	SW601193WC	227	1-320	1 0	0 0474
12-13-91	4 3 2	C2	SW601193WC	227	2-321-2	1 0	0 0126
12-13-91	4 3 2	C2	SW601193WC	227	2-321-1	1 0	0 0316
12-13-91	4 3 2	C2	SW601193WC	227	3-321-2	1 0	0 0181

These samples were traced with plutonium and processed in support of Task C

The plutonium concentrations reported in this table are the amounts of plutonium remaining after treatment. They are not the amounts of plutonium originally in the C2 pond water samples.

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Appendix 7

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	P O N D	R F SAMPLE #	SAMPLE SIZE COLLECTED LITERS	P I ID #	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L
12-13-91	4 3 2	C2	SW601193WC	227	4-321-2	1 0	0 0090
12-13-91	4 3 2	C2	SW601193WC	227	6-321-2	1 0	0 0189
12-13-91	4 3 2	C2	SW601193WC	227	3-321-1	1 0	0 0206
12-13-91	4 3 2	C2	SW601193WC	227	4-321-1	1 0	0 0040
12-13-91	4 3 2	C2	SW601193WC	227	6-321-1	1 0	0 0474
12-13-91	4 3 2	C2	SW601193WC	227	7-321-1	1 0	0 0371
12-13-91	4 3 2	C2	SW601193WC	227	1-321	1 0	0 0086
12-13-91	4 3 2	C2	SW601193WC	227	7-320-2	1 0	0 0176
12-13-91	4 3 2	N/A	SW601193WC	227	RB10414	1 0	0 0001
12-13-91	4 3 2	N/A	SW601193WC	227	RB10415	1 0	0 0002

*These samples were traced with plutonium and processed in support of Task C

The plutonium concentrations reported in this table are the amounts of plutonium remaining after treatment. They are not the amounts of plutonium originally in the C2 pond water samples.

Appendix 7

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	P O N D	R F SAMPLE #	SAMPLE SIZE COLLECTED LITERS	P I ID #	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L
12-13-91	4 3 2	C2	SW601193WC	227	2-345	2 97	0 1784
12-13-91	4 3 2	C2	SW601193WC	227	2-349	5 11	0 3004
12-13-91	4 3 2	C2	SW601193WC	227	3-346	2 88	0 1244
12-13-91	4 3 2	C2	SW601193WC	227	3-347	2 96	0 0081
12-13-91	4 3 2	C2	SW601193WC	227	3-348	2 96	0 0467

*These samples were traced with plutonium and processed in support of Task C

The plutonium concentrations reported in this table are the amounts of plutonium remaining after treatment. They are not the amounts of plutonium originally in the C2 pond water samples.

Appendix 7

Mass Spectrometric Measurements of Plutonium

DATE SAMPLED	TASK #	P O N D	R F SAMPLE #	SAMPLE SIZE COLLECTED LITERS	TEST SAMPLE SIZE (Liters)	MEASURED VALUE Pu pCi/L	Pu Am U
08-13-92	432	C2	SW60262WC1	9.5	2.0	0.0519	Pu
08-13-92	432	C2	SW60261WC2	9.5	2.0	0.0405	Pu
08-13-92	432	C2	SW60261WC1	9.5	2.0	0.0502	Pu
08-13-92	432	C2	SW60260WC2	9.5	2.0	0.0358	Pu
08-13-92	432	C2	SW60260WC1	9.5	2.0	0.0549	Pu
08-13-92	432	C2	SW60262WC2	9.5	2.0	0.0539	Pu

These samples were analyzed as part of a depth profile study of Pond C-2. The 1 affixed to the R F. Sample # denotes the first aliquot analyzed, the 2 affixed to the R F Sample # denotes the second aliquot analyzed. The Pu pCi/L values are the values observed in aliquots of three water samples collected from pond C2 on August 13, 1992.

Alpha Spectroscopy Results

Sample Number	Pond	Date Collected	Isotope	Alpha Results (pCi/L)	Analytical Uncertainty (pCi/L)
SW60171WC	A1	11/14/91	Americium-241	0 027	0 003
SW60171WC	A1	11/14/91	Plutonium-238	0 003	0 002
SW60171WC	A1	11/14/91	Plutonium-239	0 058	0 007
SW60214WC	A1	2/20/92	Plutonium-238	0 015	0 005
SW60214WC	A1	2/20/92	Plutonium-239	0 271	0 004
SW60226WC	A1	5/11/92	Plutonium-238	0 009	0 006
SW60226WC	A1	5/11/92	Plutonium-239	0 016	0 009
SW60253WC	A1	8/11/92	Plutonium-238	0 001	0 004
SW60253WC	A1	8/11/92	Plutonium-239	0 010	0 003
SW60172WC	A2	11/14/91	Americium-241	0 017	0 005
SW60172WC	A2	11/14/91	Plutonium-238	0 006	0 003
SW60172WC	A2	11/14/91	Plutonium-239	0 029	0 003
SW60215WC	A2	2/20/92	Plutonium-238	0 012	0 006
SW60215WC	A2	2/20/92	Plutonium-239	0 041	0 008
SW60227WC	A2	5/11/92	Plutonium-238	0 000	0 002
SW60227WC	A2	5/11/92	Plutonium-239	0 005	0 003
SW60234WC	A2	6/16/92	Plutonium-238	0 001	0 001
SW60234WC	A2	6/16/92	Plutonium-239	0 002	0 003
SW60252WC	A2	8/11/92	Plutonium-238	0 011	0 002
SW60252WC	A2	8/11/92	Plutonium-239	0 009	0 008
SW60173WC	A3	11/14/91	Americium-241	0 008	0 004
SW60173WC	A3	11/14/91	Plutonium-238	0 001	0 006
SW60173WC	A3	11/14/91	Plutonium-239	0 009	0 006
SW60216WC	A3	2/20/92	Plutonium-238	0 026	0 003
SW60216WC	A3	2/20/92	Plutonium-239	0 005	0 021
SW60228WC	A3	5/11/92	Plutonium-238	0 006	0 003
SW60228WC	A3	5/11/92	Plutonium-239	0 010	0 003
SW60251WC	A3	8/11/92	Plutonium-238	0 016	0 003
SW60251WC	A3	8/11/92	Plutonium-239	0 013	0 003
SW60161WC	A4	9/10/91	Americium-241	0 001	0 006
SW60161WC	A4	9/10/91	Plutonium-238	0 005	0 003
SW60161WC	A4	9/10/91	Plutonium-239	0 042	0 003
SW60165WC	A4	10/15/91	Americium-241	0 009	0 003
SW60165WC	A4	10/15/91	Plutonium -239	0 003	0 002
SW60165WC	A4	10/15/91	Plutonium-238	0 000	0 012
SW60167WC	A4	11/11/91	Americium-241	0 007	0 005

Alpha Spectroscopy Results

Sample Number	Pond	Date Collected	Isotope	Alpha Results (pCi/L)	Analytical Uncertainty (pCi/L)
SW60167WC	A4	11/11/91	Plutonium-238	0 003	0 005
SW60167WC	A4	11/11/91	Plutonium-239	0 001	0 005
SW60195WC	A4	12/17/91	Plutonium-238	0 003	0 003
SW60195WC	A4	12/17/91	Plutonium-239	0 004	0 003
SW60212WC	A4	2/20/92	Plutonium-238	0 007	0 007
SW60212WC	A4	2/20/92	Plutonium-239	0 001	0 004
SW60207WC	A4	3/17/92	Plutonium-238	0 001	0 006
SW60207WC	A4	3/17/92	Plutonium-239	0 009	0 007
SW60222WC	A4	4/20/92	Plutonium-238	0 000	0 004
SW60222WC	A4	4/20/92	Plutonium-239	0 003	0 005
SW60230WC	A4	5/13/92	Plutonium-238	0 001	0 005
SW60230WC	A4	5/13/92	Plutonium-239	0 002	0 004
SW60244WC	A4	7/22/92	Plutonium-238	0 005	0 003
SW60244WC	A4	7/22/92	Plutonium-239	0 004	0 003
SW60250WC	A4	8/11/92	Plutonium-238	0 000	0 005
SW60250WC	A4	8/11/92	Plutonium-239	0 004	0 004
SW60154WC	A4	8/27/92	Americium-241	0 002	0 005
SW60154WC	A4	8/27/92	Americium-241	0 002	0 004
SW60154WC	A4	8/27/92	Plutonium-238	0 012	0 004
SW60174WC	B1	11/14/91	Americium-241	0 115	0 004
SW60174WC	B1	11/14/91	Plutonium-238	0 019	0 004
SW60174WC	B1	11/14/91	Plutonium-239	0 218	0 004
SW60208WC	B1	2/18/92	Plutonium-238	0 007	0 003
SW60208WC	B1	2/18/92	Plutonium-239	0 292	0 005
SW60229WC	B1	5/11/92	Plutonium-238	0 001	0 007
SW60229WC	B1	5/11/92	Plutonium-238	0 002	0 002
SW60229WC	B1	5/11/92	Plutonium-239	0 039	0 005
SW60229WC	B1	5/11/92	Plutonium-239	0 044	0 013
SW60258WC	B1	8/12/92	Plutonium-238	0 010	0 003
SW60258WC	B1	8/12/92	Plutonium-239	0 028	0 003
SW60175WC	B2	11/14/91	Americium-241	0 145	0 004
SW60175WC	B2	11/14/91	Plutonium-238	0 006	0 004
SW60175WC	B2	11/14/91	Plutonium-239	0 476	0 003
SW60209WC	B2	2/18/92	Plutonium-238	0 016	0 003
SW60209WC	B2	2/18/92	Plutonium-239	0 196	0 002
SW60238WC	B2	5/14/92	Plutonium-238	0 003	0 005

Alpha Spectroscopy Results

Sample Number	Pond	Date Collected	Isotope	Alpha Results (pCi/L)	Analytical Uncertainty (pCi/L)
SW60238WC	B2	5/14/92	Plutonium-239	0 031	0 005
SW60257WC	B2	8/12/92	Plutonium-238	0 002	0 002
SW60257WC	B2	8/12/92	Plutonium-239	0 009	0 005
SW60176WC	B3	11/14/91	Americium-241	0 017	0 006
SW60176WC	B3	11/14/91	Plutonium-238	0 004	0 003
SW60176WC	B3	11/14/91	Plutonium-239	0 061	0 009
SW60210WC	B3	2/18/92	Plutonium-238	0 012	0 004
SW60210WC	B3	2/18/92	Plutonium-239	0 286	0 003
SW60239WC	B3	5/14/92	Plutonium-238	0 011	0 007
SW60239WC	B3	5/14/92	Plutonium-239	0 035	0 008
SW60177WC	B4	11/14/91	Americium-241	0 014	0 004
SW60177WC	B4	11/14/91	Plutonium-238	0 032	0 003
SW60177WC	B4	11/14/91	Plutonium-239	0 042	0 011
SW60211WC	B4	2/18/92	Plutonium-238	0 006	0 004
SW60211WC	B4	2/18/92	Plutonium-239	0 032	0 009
SW60240WC	B4	5/14/92	Plutonium-238	0 002	0 006
SW60240WC	B4	5/14/92	Plutonium-239	0 017	0 004
SW60153WC	B5	8/27/91	Americium-241	0 005	0 012
SW60153WC	B5	8/27/91	Americium-241	0 009	0 002
SW60153WC	B5	8/27/91	Plutonium-238	0 014	0 005
SW60160WC	B5	9/9/91	Americium-241	0 004	0 004
SW60160WC	B5	9/9/91	Americium-241	0 004	0 003
SW60160WC	B5	9/9/91	Plutonium-238	0 021	0 004
SW60164WC	B5	10/14/91	Americium-241	0 003	0 003
SW60164WC	B5	10/14/91	Plutonium -239	0 005	0 007
SW60164WC	B5	10/14/91	Plutonium-238	0 001	0 008
SW60168WC	B5	11/11/91	Americium-241	0 010	0 004
SW60168WC	B5	11/11/91	Plutonium-238	0 001	0 002
SW60168WC	B5	11/11/91	Plutonium-239	0 003	0 002
SW60197WC	B5	12/18/91	Plutonium-238	0.004	0 002
SW60197WC	B5	12/18/91	Plutonium-239	0 006	0 032
SW60198WC	B5	1/6/92	Plutonium-238	0 002	0 007
SW60198WC	B5	1/6/92	Plutonium-239	0 001	0 003
SW60218WC	B5	2/20/92	Plutonium-238	0 002	0 005
SW60218WC	B5	2/20/92	Plutonium-239	0 016	0 003
SW60219WC	B5	3/18/92	Plutonium-238	0 004	0 003

Alpha Spectroscopy Results

Sample Number	Pond	Date Collected	Isotope	Alpha Results (pCi/L)	Analytical Uncertainty (pCi/L)
SW60219WC	B5	3/18/92	Plutonium-239	0 031	0 005
SW60223WC	B5	4/20/92	Plutonium-238	0 010	0 006
SW60223WC	B5	4/20/92	Plutonium-239	0 005	0 025
SW60231WC	B5	5/13/92	Plutonium-238	0 000	0 003
SW60231WC	B5	5/13/92	Plutonium-239	0 006	0 020
SW60235WC	B5	6/16/92	Plutonium-238	0 002	0 006
SW60235WC	B5	6/16/92	Plutonium-239	0 008	0 024
SW60245WC	B5	7/22/92	Plutonium-238	0 007	0 002
SW60245WC	B5	7/22/92	Plutonium-239	0 007	0 011
SW60254WC	B5	8/12/92	Plutonium-238	0 001	0 003
SW60254WC	B5	8/12/92	Plutonium-239	0 006	0 006
SW60178WC	C1	11/14/91	Americium-241	0 007	0 005
SW60178WC	C1	11/14/91	Plutonium-238	0 001	0 004
SW60178WC	C1	11/14/91	Plutonium-239	0 005	0 007
SW60217WC	C1	2/20/92	Plutonium-238	0 004	0 002
SW60217WC	C1	2/20/92	Plutonium-239	0 004	0 003
SW60241WC	C1	5/14/92	Plutonium-238	0 000	0 003
SW60241WC	C1	5/14/92	Plutonium-239	0 005	0 007
SW60248WC	C1	8/11/92	Plutonium-238	0 001	0 003
SW60248WC	C1	8/11/92	Plutonium-239	0 019	0 003
SW60152WC	C2	8/28/91	Plutonium-239	0 066	0 002
SW60159WC	C2	9/9/91	Americium-241	0 009	0 003
SW60159WC	C2	9/9/91	Americium-241	0 014	0 005
SW60159WC	C2	9/9/91	Plutonium-238	0 001	0 003
SW60159WC	C2	9/9/91	Plutonium-238	0 030	0 004
SW60159WC	C2	9/9/91	Plutonium-239	0 055	0 013
SW60163WC	C2	10/14/91	Americium-241	0 015	0 007
SW60163WC	C2	10/14/91	Plutonium -239	0 044	0 004
SW60163WC	C2	10/14/91	Plutonium-238	0 001	0 002
SW60169WC	C2	11/11/91	Americium-241	0 009	0 004
SW60169WC	C2	11/11/91	Plutonium-238	0 000	0 003
SW60169WC	C2	11/11/91	Plutonium-239	0 045	0 010
SW60189WC	C2	12/12/91	Plutonium-238	0 003	0 006
SW60189WC	C2	12/12/91	Plutonium-239	0 084	0 003
SW60200WC	C2	1/6/92	Plutonium-238	0 005	0 004
SW60200WC	C2	1/6/92	Plutonium-239	0 014	0 005

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Appendix 8

Alpha Spectroscopy Results

Sample Number	Pond	Date Collected	Isotope	Alpha Results (pCi/L)	Analytical Uncertainty (pCi/L)
SW60213WC	C2	2/19/92	Plutonium-238	0 002	0 003
SW60213WC	C2	2/19/92	Plutonium-239	0 024	0 004
SW60224WC	C2	4/20/92	Plutonium-238	0 002	0 003
SW60224WC	C2	4/20/92	Plutonium-239	0 073	0 005
SW60232WC	C2	5/13/92	Plutonium-238	0 007	0 004
SW60232WC	C2	5/13/92	Plutonium-239	0 107	0 002
SW60236WC	C2	6/16/92	Plutonium-238	0 001	0 003
SW60236WC	C2	6/16/92	Plutonium-239	0 071	0 003
SW60246WC	C2	7/22/92	Plutonium-238	0 003	0 003
SW60246WC	C2	7/22/92	Plutonium-239	0 091	0 003
SW60249WC	C2	8/11/92	Plutonium-238	0 001	0 003
SW60249WC	C2	8/11/92	Plutonium-239	0 036	0 011
SW60152WC	C2	8/28/92	Americium-241	0 020	0 005
SW60152WC	C2	8/28/92	Americium-241	0 029	0 003
SW60152WC	C2	8/28/92	Plutonium-238	0 002	0 003
SW60152WC	C2	8/28/92	Plutonium-238	0 028	0 005
SW60162WC	STPEFF	9/13/91	Americium-241	0 008	0 005
SW60162WC	STPEFF	9/13/91	Americium-241	0 009	0 005
SW60162WC	STPEFF	9/13/91	Plutonium-238	0 021	0 005
SW60166WC	STPEFF	10/15/91	Americium-241	0 004	0 002
SW60166WC	STPEFF	10/15/91	Plutonium -239	0 004	0 003
SW60166WC	STPEFF	10/15/91	Plutonium-238	0.007	0 005
SW60170WC	STPEFF	11/11/91	Americium-241	0 007	0 005
SW60170WC	STPEFF	11/11/91	Plutonium-238	0 008	0 003
SW60170WC	STPEFF	11/11/91	Plutonium-239	0 000	0 009
SW60196WC	STPEFF	12/17/91	Plutonium-238	0 006	0 002
SW60196WC	STPEFF	12/17/91	Plutonium-239	0.000	0 045
SW60199WC	STPEFF	1/6/92	Plutonium-238	0 002	0 005
SW60199WC	STPEFF	1/6/92	Plutonium-239	0 002	0 002
SW60206WC	STPEFF	2/26/92	Plutonium-238	0 003	0 003
SW60206WC	STPEFF	2/26/92	Plutonium-239	0 003	0 002
SW60221WC	STPEFF	3/25/92	Plutonium-238	0 000	0 002
SW60221WC	STPEFF	3/25/92	Plutonium-239	0 005	0 007
SW60225WC	STPEFF	4/21/92	Plutonium-238	0 002	0 006
SW60225WC	STPEFF	4/21/92	Plutonium-239	0 002	0 004
SW60233WC	STPEFF	5/13/92	Plutonium-238	0 001	0 004

Alpha Spectroscopy Results

Sample Number	Pond	Date Collected	Isotope	Alpha Results (pCi/L)	Analytical Uncertainty (pCi/L)
SW60233WC	STPEFF	5/13/92	Plutonium-239	0 001	0 007
SW60237WC	STPEFF	6/25/92	Plutonium-238	0 002	0 004
SW60237WC	STPEFF	6/25/92	Plutonium-239	0 002	0 005
SW60247WC	STPEFF	7/22/92	Plutonium-238	0 004	0 002
SW60247WC	STPEFF	7/22/92	Plutonium-239	0 004	0 003
SW60259WC	STPEFF	8/12/92	Plutonium-238	0 007	0 005
SW60259WC	STPEFF	8/12/92	Plutonium-239	0 001	0 010
SW60155WC	STPEFF	8/27/92	Americium-241	0 002	0 004
SW60155WC	STPEFF	8/27/92	Americium-241	0 006	0 014
SW60155WC	STPEFF	8/27/92	Plutonium-238	0 010	0 036

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QA/QC Results for Alpha Spectroscopy

Report Number	Isotope	Analytical Result	Uncertainty	Units	QC Value	QC Uncertainty	Comments
13332	Americium-241	2.24	0.104	PC/L	2.28	0.04	Under Control
12505	Plutonium-238	2.77	0.14	PC/L	2.62	0.14	Under Control
12506	Plutonium-239	1.4	0.08	PC/L	1.34	0.02	Under Control
12507	Plutonium-238	2.77	0.14	PC/L	2.62	0.14	Under Control
12508	Plutonium-239	1.4	0.08	PC/L	1.34	0.02	Under Control
12669	Plutonium-238	0.458	0.0595	PC/L	0.44	0.02	Under Control
12670	Plutonium-239	0.351	0.0502	PC/L	0.3	0.005	Under Control
12509	Plutonium-238	2.77	0.14	PC/L	2.62	0.14	Under Control
12510	Plutonium-239	1.4	0.08	PC/L	1.34	0.02	Under Control
12668	Americium-241	2.52	0.12	PC/L	2.86	0.05	Warning 2-3 Sig
12286	Plutonium-238	0.952	0.044	PC/L	0.87	0.04	Under Control
13072	Plutonium-238	1.81	0.0771	PC/L	1.75	0.09	Under Control
13070	Plutonium-238	1.81	0.0771	PC/L	1.75	0.09	Under Control
13071	Plutonium-239	4.29	0.164	PC/L	4.45	0.08	Under Control
13073	Plutonium-239	4.29	0.164	PC/L	4.45	0.08	Under Control
13250	Americium-241	0.146	0.0202	PC/L	0.14	0.003	Under Control
13247	Americium-241	0.215	0.0178	PC/L	0.23	0.004	Under Control
13249	Americium-241	0.146	0.0202	PC/L	0.14	0.003	Under Control
13998	Plutonium-238	3.41	0.186	PC/L	3.5	0.18	Under Control
13998	Plutonium-239	0.643	0.053	PC/L	0.59	0.01	Under Control
13998	Plutonium-239	0.917	0.042	PC/L	1.04	0.02	Warning 2-3 Sig
13999	Plutonium-238	0.221	0.016	PC/L	0.24	0.01	Under Control
13247	Americium-241	0.215	0.0178	PC/L	0.23	0.004	Under Control

Samples Analyzed by Both Alpha Spectroscopy and TIMS

pic Number	Pond	Date Collected	MS Results (pCi/L)	Alpha Results (pCi/L)
1165WC	A4	10/15/91	0.0012 +/- 0.0006	0.003 +/- 0.002
57WC	A4	11/11/91	0.0041 +/- 0.0010	0.001 +/- 0.002
0195WC	A4	12/17/91	0.0009 +/- 0.0007	0.004 +/- 0.002
0207WC	A4	3/17/92	0.0199 +/- 0.0012	0.009 +/- 0.004
212WC	A4	2/20/92	0.0016 +/- 0.0008	0.001 +/- 0.003
60222WC	A4	4/20/92	0.0029 +/- 0.0007	0.003 +/- 0.003
0230WC	A4	5/13/92	0.0041 +/- 0.0010	0.002 +/- 0.003
0244WC	A4	7/22/92	0.0026 +/- 0.0007	0.004 +/- 0.003
W60250WC	A4	8/11/92	0.0025 +/- 0.0007	0.004 +/- 0.003
60164WC	B5	10/14/91	0.0032 +/- 0.0008	0.005 +/- 0.003
60168WC	B5	11/11/91	0.0055 +/- 0.0014	0.003 +/- 0.003
SW60197WC	B5	12/18/91	0.0038 +/- 0.0010	0.006 +/- 0.003
W60198WC	B5	1/6/92	0.0082 +/- 0.0005	0.001 +/- 0.003
W60218WC	B5	2/20/92	0.0067 +/- 0.0017	0.016 +/- 0.005
SW60219WC	B5	3/18/92	0.0243 +/- 0.0015	0.031 +/- 0.006
W60223WC	B5	4/20/92	0.0036 +/- 0.0009	0.005 +/- 0.009
SW60231WC	B5	5/13/92	0.0040 +/- 0.0010	0.006 +/- 0.003
SW60235WC	B5	6/16/92	0.0077 +/- 0.0019	0.008 +/- 0.004
SW60245WC	B5	7/22/92	0.0022 +/- 0.0010	0.007 +/- 0.003
SW60254WC	B5	8/12/92	0.0053 +/- 0.0013	0.006 +/- 0.004
SW60152WC	C2	8/28/92	0.0436 +/- 0.0026	0.066 +/- 0.009
SW60159WC	C2	9/9/91	0.0396 +/- 0.0024	0.055 +/- 0.009
SW60163WC	C2	10/14/91	0.0475 +/- 0.0029	0.044 +/- 0.007
SW60169WC	C2	11/11/91	0.0304 +/- 0.0018	0.045 +/- 0.008
SW60189WC	C2	12/12/91	0.0209 +/- 0.0013	0.084 +/- 0.011
SW60200WC	C2	1/6/92	0.0126 +/- 0.0008	0.013 +/- 0.005
SW60213WC	C2	2/19/92	0.0202 +/- 0.0012	0.024 +/- 0.008
SW60224WC	C2	4/20/92	0.0510 +/- 0.0031	0.073 +/- 0.011
SW60232WC	C2	5/13/92	0.0966 +/- 0.0029	0.107 +/- 0.013
SW60236WC	C2	6/16/92	0.0623 +/- 0.0037	0.071 +/- 0.010
SW60246WC	C2	7/22/92	0.0799 +/- 0.0048	0.091 +/- 0.013
SW60249WC	C2	8/11/92	0.0342 +/- 0.0021	0.036 +/- 0.007
SW60166WC	STPEFF	10/15/91	0.0027 +/- 0.0014	0.004 +/- 0.004
SW60170WC	STPEFF	11/11/91	0.0008 +/- 0.0008	0.000 +/- 0.002
SW60196WC	STPEFF	12/17/91	0.0015 +/- 0.0008	0.000 +/- 0.003
SW60199WC	STPEFF	1/6/92	0.0036 +/- 0.0009	0.002 +/- 0.005
SW60206WC	STPEFF	2/26/92	0.0013 +/- 0.0007	0.003 +/- 0.003
SW60221WC	STPEFF	3/25/92	0.0025 +/- 0.0006	0.005 +/- 0.003
SW60225WC	STPEFF	4/21/92	0.0005 +/- 0.0009	0.002 +/- 0.002
SW60233WC	STPEFF	5/13/92	0.0018 +/- 0.0009	0.001 +/- 0.002